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Comparison of the Angular Distributions of the Cosmic Radiation at Elevations 6280 ft. and 620 ft.

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(Received January 17, 1933)

The ray intensity $j(\theta)$ of the cosmic radiation has been studied as a function of the angle θ from the vertical on Mt. Washington, New Hampshire, elevation 6280 ft. and at a base station, elevation 620 ft. The results show a distribution less concentrated about the vertical at the higher elevation. Unless some *ad hoc* assumption is invoked this result is inconsistent with the intensities and absorption coefficients deduced by Millikan and Cameron as their results would lead to a considerably more concentrated distribution at the upper elevation. Integrating the ray intensities over all angles, the total numbers of rays per cm² per sec. have been computed at the two elevations. The increase in the number of rays with elevation is less than the known increase in the ionization (Millikan and Cameron). The ratio of numbers of rays per sec. is 1.46 against 1.91 for the ratio of ionizations at the two elevations. The average 6280 ft. ray, therefore, produces 1.31 as many ions per unit path as the 620 ft. ray. This change in ionizing efficiency may perhaps be explained by supposing that the softer rays, which are more predominant at the upper level, produce more secondary rays from the walls of the ionization vessel.

ALTHOUGH the angular distribution of the cosmic radiation at a single elevation has been measured by Bernardini,[1] Medicus,[2] Tuwim,[3] Skobelzyn[4] and others, it is believed that the measurements herein reported are the first to show the changes in this distribution with elevation. The relative intensities of the radiation at various angles from the vertical have been measured on Mt. Washington, New Hampshire, elevation 6280 ft. and at a nearby station in Maine, elevation 620 ft., under conditions such that the results at the two elevations may be compared.

On the basis of the simple theory which neglects magnetic effects and scattering, and assumes an isotropic distribution of the radiation at the top of the atmosphere, the intensity, $j_i(\theta)$, of a component of the radiation (defined as the number of rays per unit solid angle per cm² per sec.) of which the absorption coefficient is μ_i, is a function of the directions of its path through the atmosphere. At a depth h from the top of the atmosphere the intensity at angle θ from the vertical should be given by

$$j_i(\theta) = j_{oi} e^{-\mu_i h \sec\theta}. \quad (1)$$

The total intensity at angle θ is therefore given by the sum of a series of such terms corresponding to the various components of the primary radiation.

$$j(\theta) = \Sigma j_i(\theta). \quad (2)$$

Since secondary rays are also included in the measurements, this theory cannot be rigorously exact for undoubtedly the secondaries do not always follow the directions of the primary rays

[1] G. Bernardini, Nature **129**, 578 (1932).
[2] G. Medicus, Zeits f. Physik **74**, 350 (1932).
[3] L. Tuwim, Berlin Berichte **19**, 91, 360 (1931).
[4] D. Skobelzyn, Comptes Rendus **194**, 118 (1932).

which produce them, and some large angle scattering of the primary rays may also take place. Therefore, the measured distribution must be less concentrated about the vertical than that represented by (2). For this reason it would be futile to deduce values of j_{oi} and μ_i from the present data, although this would be possible on the basis of the above simple assumptions.

The apparatus consisted of three Geiger-Mueller counters mounted in line (Fig. 1) and

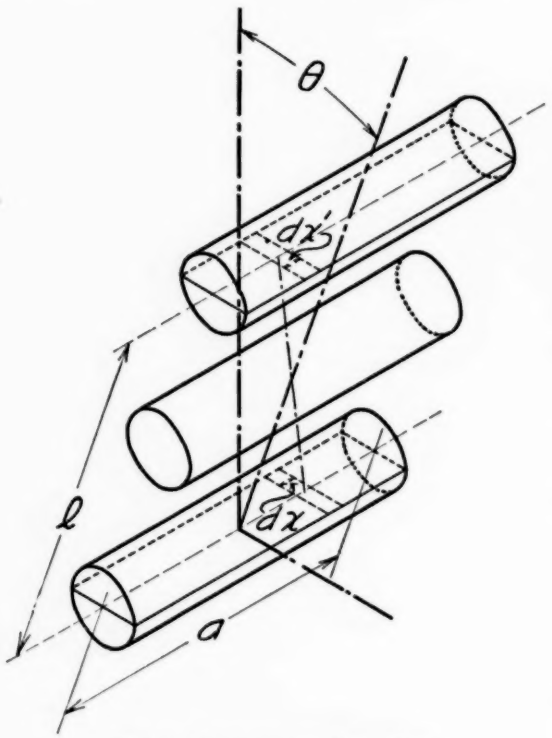

FIG. 1. Arrangement of counters.

connected for recording triple coincidences.[5] The counters were cylindrical, 12.7 cm long and 3.8 cm in diameter and were spaced 10 cm between adjacent axes. The cross-sectional area of the sensitive volume was determined by comparing the coincidence counting rate of these counters with that of a pair of counters specially constructed to eliminate end corrections. The resulting sensitive areas, assumed rectangular, were 8.8 cm by 3.8 cm. This method for making end corrections is not entirely satisfactory as it does not take account of the relative efficiencies of the two sets of counters. For the purpose at hand, however, it is sufficiently accurate, since the length of the sensitive volume enters the computations only through a small correction term.

Observations were made with the line of the counters pointing towards the magnetic south at various inclinations from the vertical. Readings were taken and the inclination changed at the end of approximately three hour intervals. A summary of the results is contained in Table I,

TABLE I. *Summary of observations.*

θ	n	T	C	r	R	R'	f	j
Mt. Washington, elevation 6280′, mean barometer 590.5 mm								
0°	6	1100	2789	2.54	0.046	0.033	0.00650	0.0165
20°	9	1487	3256	2.19	.024	.026	.00648	.0142
30°	5	909	1662	1.83	.031	.030	.00644	.0118
40°	7	1185	1635	1.38	.024	.028	.00642	.0089
60°	6	987	532	0.54	.013	.016	.00636	.0034
80°	5	1106	120	0.11	.002	.006	.00632	.00069
90°	3	664	28	0.04	.003	.005	.00632	.00025
Base station, elevation 620′, mean barometer 748 mm								
0°	8	1637	2940	1.80	0.015	0.022		0.0117
20°	5	1058	1570	1.49	.019	.025		.00966
30°	5	1198	1381	1.15	.016	.021		.00741
40°	5	1032	892	0.86	.008	.019		.00552
60°	4	729	251	0.35	.013	.015		.0022
80°	4	707	33	0.05	.005	.005		.00032
90°	1	181	8	0.04		.01		.00025

which gives, for each inclination, the number of runs n, the total time in minutes T, the total number of counts C, and the number of counts per minute r. The probable error of r as estimated from the residuals is given in the table under R.

$$R=0.6745[\Sigma v^2/(n-1)n]^{\frac{1}{2}}.$$

If no instrumental variations are present and the cosmic rays are of constant intensity, the variations should be just those arising from the statistical fluctuations. The probable error should, therefore, depend only on the number of counts C, and its value should be $R'=0.6745\times C^{\frac{1}{2}}/T$. The values of R' are also included in the table and the agreement of R and R' is an indication of the reliability of the result. This agreement is good in every case with the possible exception of the Mt. Washington 0° value and, even there, the discrepancy is not great enough to definitely indicate trouble. For cases in which

[5] T. H. Johnson and J. C. Street, J. Franklin Inst., March, 1933.

R is less than R' the latter is the more accurate value.

Since the solid angle subtended by the counters was small, the counting rates, $r(\theta)$, are, to a fairly close approximation, proportional to the intensity $j(\theta)$, θ referring to the inclination of the line of centers of the counters. (Fig. 1.) There is, however, a small geometrical correction having a maximum variation with θ of 3 percent, which can be determined by an integration extending over the areas of the two extreme counters. Over the small range of inclinations of lines joining points on the axes of the two extreme counters, it has been assumed, for the purpose of the integration, that the intensity varies as the square of the cosine of the inclination from the vertical, this law being approximately correct empirically. Furthermore, if it be assumed that the variation of j is linear over the short range of angle subtended by the diameters of the extreme counters, integration along this dimension becomes unnecessary and the total number of rays per second passing through all three counters when pointing in the vertical direction ($\theta=0$) is given by

$$r(0)=j(0)d^2l^4\int_{-a'/2}^{+a'/2}\int_{-a/2}^{+a/2}dx'dx/[(x-x')^2+l^2]^3$$
$$=j(0)/F(0).$$

Here d is the diameter, a' and a are the lengths of the two extreme counters, and l is the distance between the extreme axes. Since the inclinations of lines joining axial points of the two extreme counters vary less and less with increasing inclination of the line joining the centers, the factor in the integral which takes account of the change of intensity of the radiation over the range of angles subtended by lengths of the counters becomes equal to unity for θ equal to $\pi/2$ and

$$r(\pi/2)=j(\pi/2)d^2l^2\int_{-a'/2}^{+a'/2}\int_{-a/2}^{+a/2}\frac{dx'dx}{[(x-x')^2+l^2]^2}$$
$$=j(\pi/2)/F(\pi/2).$$

For intermediate angles it is easy to show that

$$j(\theta)=r(\theta)F(\pi/2)(1+\epsilon\cos^2\theta)=r(\theta)f(\theta),$$

where $\epsilon=F(0)/F(\pi/2)-1$. The factors $f(\theta)$ are given in the tables as also are the corresponding values of $j(\theta)$. These values of $j(\theta)$ are still not strictly equal to the intensities, for the efficiency of the counters has not been measured and the end corrections are not accurately known. They are, however, proportional to the intensities at a single elevation. Before comparing the results at the two elevations it is necessary to investigate possible changes in the efficiency with the counting rate of the individual counters, since this changed from 100 per min. at the base station to 200 per min. on Mt. Washington.

For the purpose of this investigation the triple coincidence counting rate has been measured in the laboratory with the individual counting rates controlled by the proximity of a tube of radium emanation. These measurements consisted of a series of 34 determinations of the triple counting rates with the individual counting rates alternated between 85 per min. and 197 per min. The measurements satisfied the $R=R'$ criterion and they showed the change in coincidence counting rate to be less than the probable error (2.5 percent). Therefore, no further correction to the j values listed in the table need be applied to make them comparable at the two elevations.

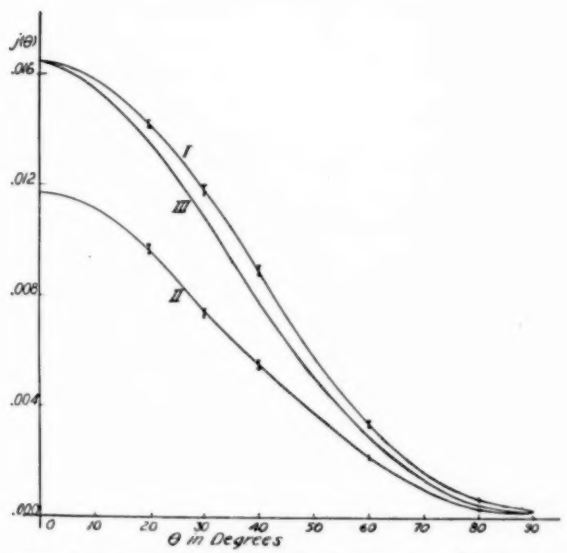

FIG. 2. Intensity of cosmic rays as function of inclination to the vertical. I. Elevation 6280 ft. II. Elevation 620 ft. III. II×1.41.

In Fig. 2, $j(\theta)$ has been plotted against θ. Curve I represents the Mt. Washington values, curve II the values at the base station and curve III has been computed by multiplying II by a

constant factor. A comparison of I and III shows that the distribution is broader at the higher elevations. This is contrary to the change one would have expected on the basis of the intensities and absorption coefficients deduced by Millikan and Cameron[6] as they would have lead, on the assumptions of the simple theory, to a considerably sharper distribution at the higher elevation. The distribution at the lower elevation, however, is in good agreement with their intensities and absorption coefficients and the discrepancy at the higher elevation arises from the very intense soft component which they have deduced.

Another point of apparent inconsistency between the ionization-intensity measurements and the ray-intensity measurements is the difference in their respective variations with elevation.

The ray-intensity, J, defined as the total number of rays per cm² per second from all directions, is given by

$$J = 2\pi \int_0^{\pi/2} j(\theta) \sin\theta \cos\theta d\theta.$$

The integration has been performed graphically with the results

$$J_{6280} = 0.024 \text{ rays per cm}^2 \text{ per sec.}$$

$$J_{620} = 0.016 \quad " \quad " \quad " \quad " \quad "$$

$$J_{6280} : J_{620} = 1.46.$$

The ionization-intensities I, defined as the number of ions per cc per sec. produced by the cosmic radiation in an unshielded electroscope were computed for the barometric pressures experienced on Mt. Washington and at the base station by interpolation from the values given by Millikan and Cameron.[6] The values are:

$$I_{6280} = 70.0 \text{ ions per cc per sec.}$$

$$I_{620} = 36.7 \quad " \quad " \quad " \quad " \quad "$$

$$I_{6280} : I_{620} = 1.91.$$

It appears, therefore, that the average ray at 6280 ft. has $(1.91 \div 1.46)$ 1.31 times the ionizing efficiency of the average ray at 620 ft. elevation.

As a possible interpretation of the latter discrepancy between the ionization-intensity and ray-intensity measurements, it is suggested that the softer radiation which predominates at the higher elevations may have the greater tendency to produce groups of secondary rays in the walls of the ionization vessel. If this interpretation is correct the experiments, such as that of Schindler,[7] would be expected to show greater "übergangseffekte" at higher elevations and it would imply that the cosmic-ray ionization as measured in a closed vessel would depend upon the wall thickness and the nuclear constitution of the wall material in a way which varies with the elevation. The unexpected broader distribution at the higher elevation may have its explanation in a more predominant large angle scattering on the part of the soft rays.

The calculations are, of course, based upon the assumption of a uniform azimuthal distribution and the results would be affected by any departures from uniformity such as are indicated by the measurements on Mt. Washington made by the writer in collaboration with J. C. Street.[8]

It is a pleasure to acknowledge the cooperation of J. C. Street in developing and building the apparatus and in taking some of the readings. The writer is also indebted to H. N. Teague and Myron E. Witham of the Mt. Washington Club for the use of Camden Cottage in which the measurements on Mt. Washington were made.

[6] R. A. Millikan and C. H. Cameron, Phys. Rev. **37**, 235 (1931).

[7] H. Schindler, Zeits. f. Physik **72**, 625 (1931).

[8] T. H. Johnson and J. C. Street, Minutes of the Atlantic City Meeting of the Am. Phys. Soc. December, 1932.

Measurement of the Range of Alpha-Particles from Thorium with the Wilson Chamber

F. N. D. KURIE * AND G. D. KNOPF, *Sloane Physics Laboratory, Yale University*

(Received January 13, 1933)

The range of the α-particles from thorium has been measured by the methods used by one of the authors previously. At 0°C and 760 mm the extrapolated number-distance range is 2.72 ± 0.03 cm. This range is derived from 300 tracks. It is pointed out that the great deviation of this range from that of Henderson and Nickerson is partially due to these authors' treatment of their data. The Geiger-Nuttall law is shown in the form indicated by Gamow's theory, and the latest data for the uranium and thorium series pertaining to it are given.

INTRODUCTION

THE range of the α-particles from thorium has been measured only twice, and in both these measurements the degree of uncertainty was rather large. Until recently the only reliable determination was that of Geiger and Nuttall,[1] which was recalculated later by Geiger[2] to be 2.75 cm at 0°C and 760 mm. The experiment consisted in measuring the current between the source placed at the center of a sphere and the sphere as a function of pressure. The range was then calculated from the point at which the particles are no longer absorbed completely in the gas. This is essentially an extrapolated ionization range.

The only other measurement of importance is that of Henderson and Nickerson[3] who used the cloud chamber method of G. C. Laurence.[4] Their low value of 2.46 cm may be partially accounted for by the manner in which these authors treat their data. This point will be considered more fully later.

EXPERIMENTAL PROCEDURE AND RESULTS

The method used has been described by one of us in another paper.[5] Briefly it consists of taking two photographs of the tracks due to the α-particles in question formed in a large Wilson cloud chamber and from them constructing a replica of the original track. This replica is measured and reduced to standard conditions (0°C, 760 mm).

The source was prepared from commercial metallic thorium by grinding it into a fine powder, shaking it with chloroform to get only the finest particles in suspension and pouring it over a sheet of mica held to the base of a flat dish. As the chloroform evaporates it deposits the silt of thorium metal as a very uniform layer on the mica. This mica sheet is then mounted in the center of the cloud chamber. The source was quite thick, equivalent to around 10 mm of air. This thickness causes the number-distance curve of thorium to overlap that of ionium, which is present as an isotopic impurity. The method of plotting on probability paper suggested by one of us[6] allows the separation of the thorium curve from the ionium curve to be made in a direct manner so that thick sources may be used with nearly the same accuracy as thin ones. In this case a balance had to be struck between the accuracy aimed at and the amount of time to be devoted to the experiment. It was found that, since the correction to be applied for thickness of source is the same for one of two equivalent mm of air as for one infinitely thick, the time factor was the more important. A source 10 mm of air thick was found to give a sufficiently great number of tracks without spreading the number-distance curves excessively.

* Sterling Fellow.

[1] H. Geiger and J. M. Nuttall, Phil. Mag. [6] **22**, 613 (1911).

[2] H. Geiger, Zeits. f. Physik **8**, 45 (1922).

[3] G. H. Henderson and J. L. Nickerson, Phys. Rev. **36**, 1344 (1930).

[4] G. C. Laurence, Phil. Mag. [7] **5**, 1027 (1928).

[5] F. N. D. Kurie, Rev. Sci. Inst. **3**, 655 (1932).

[6] F. N. D. Kurie, Phys. Rev. **41**, 701 (1932).

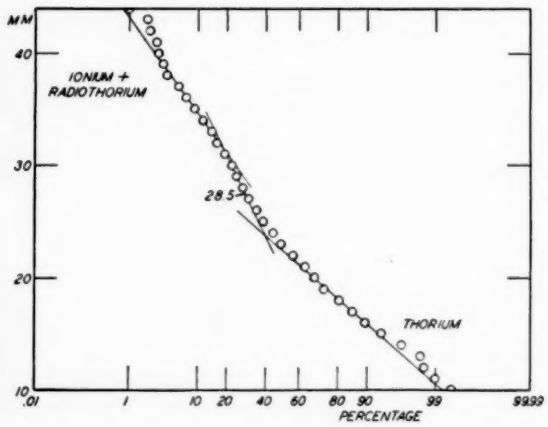

FIG. 1. Number-distance curve for thorium α-particles drawn on probability paper. When the section above 28.5 percent is plotted separately one gets a straight line showing that it corresponds to a simple group of α-particles (thorium). When the section below 28.5 percent is plotted separately, it splits again into groups corresponding to ionium and radiothorium.

No attempt was made to purify the thorium in any way, since the elements whose α-particles have ranges nearest to thorium are ionium (3.03 cm) and radiothorium (3.81 cm) which are isotopes of thorium, and cannot be separated from it chemically. The other elements in the series emit α-particles of so much longer ranges that they can be easily recognized.

Some 1200 tracks of thorium-ionium-radiothorium were photographed, of which 300 were sufficiently sharp to be measured. Their lengths were reduced to standard conditions. The final data are shown in Fig. 1 as a number-distance curve plotted on probability paper. It consists of three portions corresponding to the major separation into thorium and ionium + radiothorium. The midpoint of the short connecting line is the fraction of these two groups. Thus the ionium + radiothorium group is 28.5 percent of the total number of tracks. Another probability paper plot of the lower 28.5 percent gives two further splits at 22.5 percent and 3.3 percent corresponding to ionium and radiothorium respectively.

The ranges, then, are the intersections of the linear portions of the number-distance curves with these various percentages which represent the no-particle lines of the different groups of α-particles as shown in Fig. 2. Uncorrected for absorption in the source, these are: thorium, 2.67 cm; ionium, 2.97 cm; radiothorium, 3.76 cm. The correction to be applied is given by Laurence[4] and is $\alpha\pi^{\frac{1}{2}}/2$, where α is the straggling coefficient. The straggling coefficients are 0.050 cm, 0.055 cm and 0.070 cm for thorium, ionium and radiothorium, respectively, so that the corrections to be added are 0.044 cm, 0.049 cm and 0.062 cm.

The final corrected range of thorium at 0°C and 760 mm is $R_{\mathrm{Th}}=2.72\pm0.03$ cm. The limit of reliability is got by assigning to each column in the distribution histogram, which is shown in outline in Fig. 2, the error appropriate to the number of particles it contains. From the two limiting number-distance curves so obtained one gets the extreme ranges $R_0\pm p$ where p is the limit of reliability. To this is added an error of one percent in the determination of the no-particle line, which corresponds to 0.01 cm in the range.

The corrected ranges for ionium and radiothorium are 3.03 cm and 3.83 cm which are to be

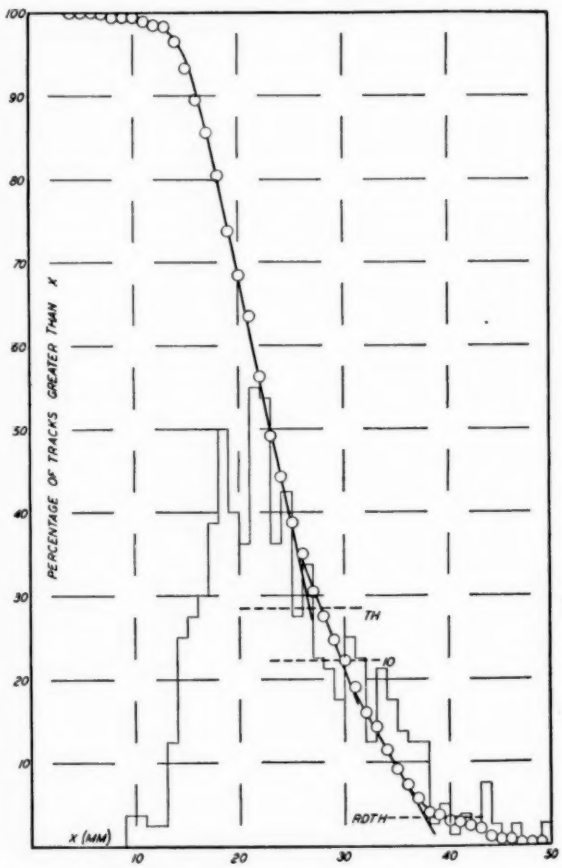

FIG. 2. Number-distance curve for thorium α-particles. In outline is shown the distribution histogram of the track lengths. The dotted lines are drawn corresponding to the percentages obtained from plots on probability paper.

compared with the standard values of 3.03 cm and 3.81 cm. Because of the very few tracks from which these ranges are deduced they must not be regarded as anything but non-contradictory evidence.

Discussion

It is difficult to account for the difference between the value of 2.45 cm got by Henderson and Nickerson and the present value which is very near that of Geiger. If the data of these authors as given in Fig. 1 of their paper[3] be plotted on probability paper in order properly to ascertain the no-particle line of the thorium group the range is found to be 2.58 cm at 0°C, 760 mm which accounts for half the discrepancy. It cannot be too often repeated that the range of a group of α-particles is by definition the point of intersection of the linear portion of the number-distance curve with the no-particle line of that group. When the number-distance curves of two groups overlap as they do in the thorium-ionium pair, a complete separation must be made before the range of the shorter may be deduced. The only method known to us is by the use of plots on probability paper, and that has been found to be accurate to one percent.

The Geiger-Nuttall Law

The theory of radioactive disintegration due to Gamow[7] leads to a relation between the disintegration constant λ and the energy of the disintegration E of the form

$$\log \lambda = a_{01} - a_{11}(E)^{-\frac{1}{2}}. \qquad (1)$$

The constants a_{01} and a_{11} are functions of the atomic number and the radius of the nucleus which vary very slowly from element to element. They are calculable from the theory if one assumes a value of the radius, and this may be done approximately. This relation is the quantum mechanical successor to the Geiger-Nuttall law. If one plots $\log \lambda$ against $(E)^{-\frac{1}{2}}$, one gets a straight line as shown in Fig. 3. This line is a least squares fit to the data given in Table I, which contains what we consider the most reliable information about the uranium and thorium series.

[7] G. Gamow, *Constitution of Atomic Nuclei and Radioactivity*, p. 50. Oxford, 1931.

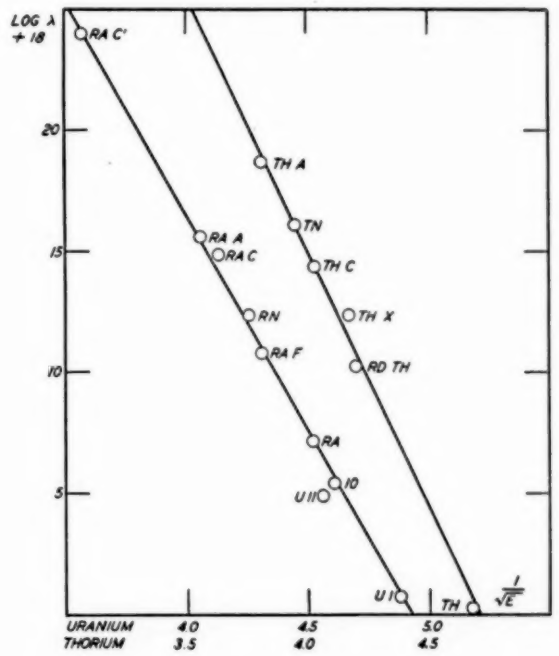

Fig. 3. The Geiger-Nuttall relation in the form suggested by Gamow's theory. The units of the disintegration constant λ are sec.$^{-1}$ and those of the energy of disintegration E are 10^8 electron-volts.

The ranges of uranium I, uranium II, polonium and thorium are those of Kurie[6]; the ranges of ionium, radium, radiothorium and thorium X are those of Geiger[2]; the ranges of radon, radium A, radium C', thorium C, thoron and thorium A are those of Lewis and Wynn-Williams[8]; the

Table I.

Substance	Extrapolated ionization range (cm at 0°C, 760 mm)	Energy of disintegration (elect.-volts $\times(10)^{-6}$)	Disintegration constant (sec.$^{-1}$)
U I	2.57	4.21	$4.86(10)^{-18}$
U II	3.10	4.78	$7.4(10)^{-14}$
Io	3.03	4.70	$2.6(10)^{-13}$
Ra	3.21	4.90	$1.38(10)^{-11}$
Ra C	4.1	5.85	$5.86(10)^{-4}$
Ra F	3.68	5.39	$5.73(10)^{-8}$
Rn	3.848	5.54	$2.10(10)^{-6}$
Ra A	4.430	6.07	$3.78(10)^{-3}$
Ra C'	6.583	7.83	$(10)^{6}$
Th	2.71	4.56	$1.7(10)^{-18}$
RdTh	3.81	5.51	$1.16(10)^{-8}$
Th X	4.13	5.77	$2.20(10)^{-6}$
Th C	4.485	6.16	$1.91(10)^{-4}$
Tn	4.761	6.38	$1.27(10)^{-2}$
Th A	5.369	6.88	4.95

[8] W. B. Lewis and C. E. Wynn-Williams, Proc. Roy. Soc. **A136**, 349 (1932).

range of radium C is that of Rutherford, Ward and Wynn-Williams.[9] The disintegration constants are those given in the Report of the International Radium Standards Commission,[10] with the exception of uranium I,[11] which is that of Kovarik and Adams, and thorium. Unpublished work by A. F. Kovarik and N. I. Adams, Jr., in this laboratory indicates that λ for thorium is more nearly that given by Geiger and Rutherford[12] than that of Kirsch[13] so the former's value is here taken. The energies of disintegration have been caculated from the ranges with due regard to the deviations from Geiger's law relating velocity to range and have been corrected for recoil.

[9] Lord Rutherford, F. A. B. Ward, C. E. Wynn-Williams, Proc. Roy. Soc. **A129**, 211 (1930).

[10] Rev. Mod. Phys. **2**, 427 (1931).

[11] A. F. Kovarik and N. I. Adams, Jr., Phys. Rev. **40**, 718 (1932).

[12] H. Geiger and E. Rutherford, Phil. Mag. [6] **20**, 691 (1910).

[13] G. Kirsch, Wien. Ber. **131**, 551 (1922).

For the uranium series the best straight line is given by

$$\log \lambda = 69.58 - 17.79(E)^{-\frac{1}{2}} \tag{2}$$

and for the thorium series by

$$\log \lambda = 83.13 - 21.51(E)^{-\frac{1}{2}}. \tag{3}$$

In these equations λ is measured in sec.$^{-1}$ and E in $(10)^8$ electron-volts. According to Gamow's theory, if one takes a mean atomic number of 82.5 and a value for the radius of the nucleus of $8(10)^{-13}$ cm, the predicted relation is approximately

$$\log \lambda = 53.3 - 14.2(E)^{-\frac{1}{2}}. \tag{4}$$

There is very little agreement between the coefficients in the predicted and observed lines, but it is clear from Fig. 3 that the *form* of the relation is a close approximation to the facts. It is perhaps significant that the ratio $a_{01} : a_{11}$ is very nearly 4 in all cases.

The Continuous Absorption of Oxygen Between 1750 and 1300A and Its Bearing Upon the Dispersion

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In connection with recent measurements of the dispersion of oxygen down to 1920A, the continuous absorption of oxygen between 1750 and 1300A has been investigated quantitatively with a small fluorite spectrograph by the photographic-photometric method. The results are given in a graph, which shows that the absorption coefficient α as function of the wave number ν has a relatively sharp maximum at 6.8×10^4 cm^{-1} ($\lambda=1450$A) and falls off rather symmetrically on both sides. The maximum absorption coefficient reduced to N.P.T. is about 490 cm^{-1}. The absorption in this region of the spectrum is so strong that during a few minutes exposure a great part of the oxygen disappears, being dissociated and probably absorbed by the metal walls of the tube. By integration of the absorption curve one gets the corresponding f-value according to the equation $\int\alpha(\nu)d\nu=\pi Nfe^2/mc^2=(2.38\times10^7)f$. The f-value calculated from this expression is 0.193 compared with 0.202 calculated from the dispersion measurements. The corresponding resonance wave-length from the dispersion measurements is 1468 in fairly good agreement with the observed position of the maximum of absorption. A dispersion formula which takes into account the distribution of absorption in a continuous band is given, and is applied to the dispersion of oxygen.

IN a recent paper, Ladenburg and Wolfsohn have shown,[1] that the dispersion of oxygen between the visible and 1920A can be described quantitatively by three resonance wave-lengths $\lambda_1=1899$A, $\lambda_2=1468$A and $\lambda_3=544$A, with the three corresponding "strengths" (number of oscillators per atom) $f_1=4.0\times10^{-5}$, $f_2=0.202$ and $f_3=5.93$.

λ_1 can be ascribed to the Schumann-Runge band $v''=0\rightarrow v'=5$ the head of which lies at 1903A, and has according to its very small f value only a slight influence upon the dispersion and only in the region up to 1960A. The influence of the even weaker bands[2] (0.4), (0.3) ··· at 1923, 1945 ··· seems to be negligible. The resonance wave-length λ_2 has obviously to be attributed to the continuous absorption on the short wave-length side of the Schumann-Runge bands which sets in at 1750A. In order to learn more about this absorption as well as about the even stronger absorption at lower wave-lengths $-\lambda_3$ being $=544$A and $f_3=5.93$, i.e., approximately 30 times as large as f_2, we have investigated the absorption of oxygen by means of vacuum spectrographs, partly in collaboration with J. C. Boyce. A preliminary account of these investigations was published some months ago.[3] The qualitative experiments carried through by means of the 2 meter vacuum grating spectrograph, designed by Drs. K. T. Compton and J. C. Boyce, showed strong absorption of oxygen from 1100A down and still quite strong at 300A, the estimated maximum of which is in fair agreement with the resonance wave-length.

A more complete account of our experiments on the continuous absorption spectrum of oxygen between 1750 and 1300A and of its bearing upon the dispersion is the subject of this paper.

Apparatus and Experimental Procedure

Spectrograms recording the O_2 absorption were obtained by the use of a hydrogen discharge tube, which gives many strong lines in the spectral region investigated, an absorption cell with suitable diaphragms, and a Cario and Schmidt-Ott fluorite spectrograph,[4] all connected together with white wax as shown in Fig. 1. The H_2 discharge tube was constructed of Pyrex glass and had a water-cooled capillary about 5 mm inside diameter and 17.5 cm long, coated inside

[1] R. Ladenburg and G. Wolfsohn, Zeits. f. Physik **79**, 42 (1932).

[2] Cp. W. Weizel, Handb. Experimental-Physik, Ergänzungsband I, 366 (1931).

[3] R. Ladenburg, C. C. Van Voorhis and J. C. Boyce, Phys. Rev. **40**, 1018 (1932) (Letter to the Editor).

[4] G. Cario and H. D. Schmidt-Ott, Zeits. f. Physik **69**, 719 (1931).

with a layer of silver so thin that it conducted practically none of the electric current. Electrolytic hydrogen dried over P_2O_5 was used in the discharge tube at about 1 mm pressure, a 5 liter flask serving as a stabilizing reservoir during a run.[5] The electrodes were aluminum hollow

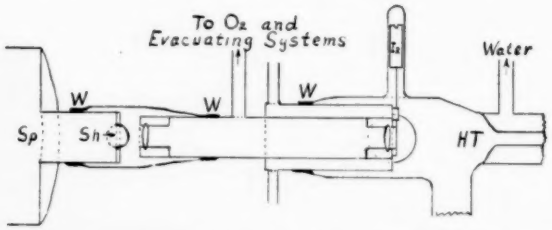

FIG. 1. Connections between hydrogen tube *HT*, absorption tube and spectrograph *Sp*.

cylinders 8 cm long and 4 cm in diameter and the direct current of from 15 to 100 milliamperes was supplied by a 3000 volt motor-generator set run on a large storage battery to ensure constant current.[6] Beakers of water surrounding the electrode chambers prevented overheating of the electrodes. To allow for the use of a quartz mercury lamp in adjusting the optical system a quartz plate was sealed to one end of the discharge tube. The other end of the discharge tube was provided with the necessary openings and side tubes for waxing in the absorption chamber and mounting the set of diaphragms and its controls. Fig. 2 shows in detail the construction of the absorption chamber and diaphragm system. The absorption chamber whose length between lenses was 12.3 cm was made of brass and all parts were nickel-plated after being fabricated. The fluorite lenses *F* were waxed into the ends of the chamber with white wax. The caps C_1 and C_2 and lead washers *L* serve to hold the lenses in place, thus relieving any strains on the wax when there is high pressure in the absorption chamber and low pressure in the discharge tube and spectograph. The cap C_2 was fastened with set screws to allow for the proper orientation of the diaphragm carrier which it also supports. To prevent possible heating to the softening point of the wax in the end sealed into the H_2 discharge tube this end was surrounded by a water jacket constructed as shown in Fig. 2. Though this end enters the discharge tube the resistance of about 10 meters of tap water flowing through rubber tubing was enough to prevent any appreciable discharge to the absorption tube when the nearest electrode was grounded.

The set of diaphragms consisted of five with relative open spaces for *a*, *b*, *c*, *d* and *e* of 1.000, 0.494, 0.244, 0.131 and 0.062 (accuracy within 2 percent) respectively, as determined with a projector lamp, thermopile and galvanometer. The diaphragms were mounted in a carrier with the openings symmetrical about the vertical axis as shown in Fig. 2. The diaphragm carrier slid in grooves in cap C_2 thus allowing each diaphragm to be brought into position in front of the lens and very close to it, by means of a solenoid acting on the soft iron rod I_1 which slid in a horizontal glass side tube of the discharge tube. The spring *S* in an opposite horizontal side tube and the ratchet *R* catching in the notches *N* served to locate the diaphragms exactly in front of the lens, the ratchet being lifted at will by another solenoid around I_2 in a third side tube rising vertically.

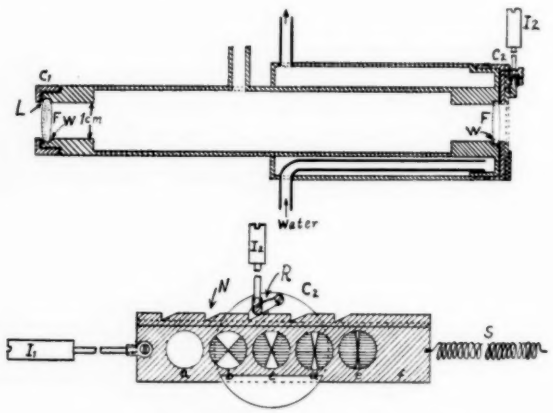

FIG. 2. Absorption tube and diaphragms.

The end of the discharge tube receiving the one end of the absorption tube and the diaphragm system was so dimensioned as to locate the lens about 5.5 cm from the near end of the discharge tube capillary. The spectrograph was so placed that the slit was about 6.0 cm from the

[5] As there are no strong hydrogen lines above $\lambda = 1645$A we used the CO lines obtained by adding a slight amount of CO_2 to the hydrogen for investigating the longer wavelengths.

[6] Direct current is important for photographic-photometric measurements.

second lens of the absorption tube, 6.0 cm being the focal length of each lens for $\lambda = 1450$.

The O_2 used in the absorption chamber was prepared by the electrolysis of dilute H_2SO_4 and dried over P_2O_5; the pressure of the O_2 giving suitable results was between 1.86 mm and 0.079 mm (Hg).

Eastman Type 3-0 Ultra Violet Sensitive Plates[7] were used in the spectrograph because though the grain was coarser than in Nujol-sensitized Cramer Contrast Plates the former were likely to be more uniform over the whole area of the plate than the latter. After exposure the plates were rinsed in acetone to remove the sensitizing dye and were then developed for three minutes in 1 to 20 Rodinal solution. Seven spectrograms could be made on each plate.

The following is the procedure used in making the spectrograms. After running the H_2 discharge tube for a half-hour or more to obtain constant conditions, four or five exposures were made for a given length of time, each with a different diaphragm in front of the absorption chamber. Then the three (or two) remaining exposures were made for the same length of time with the fully open diaphragm *a* in position and suitable pressures of O_2 in the absorption chamber. Thus under proper conditions two or three independent sets of results could be obtained from each plate. The times of exposure for different plates varied in our work from 20 to 120 seconds with a possible timing error of less than 0.4 second, a magnetically-operated sliding shutter *Sh* (Fig. 1) serving to open and close the spectrograph.

Rather large discrepancies appeared in the earlier results, some of which were obtained with the volume of O_2 in communication with the absorption tube small (about 30 cc) because of a nearby stopcock being closed, and others with the much larger volume of the McLeod gauges, liquid air trap and connecting tubing, i.e., about 425 cc, in communication. These discrepancies were found to be due to a very large "clean up" action in O_2 produced by light in this region of the spectrum. This disappearance of O_2 molecules is attributed to their optical dissociation by the short wave-lengths and presumably to consequent adsorption or chemical action on the metal surface of the absorption chamber or to the formation of O_3. The spectrograms whose positives are reproduced in Fig. 3 illustrate this clean up effect. Spectrograms 1, 2, 3 and 4 were taken with diaphragms *a*, *b*, *c* and *d*, respectively, then 5 was made, with diaphragm *a* in place, immediately after the 425 cc volume had been filled with O_2 at 0.27 mm pressure, and 6 and 7 were made 3 and 20 minutes, respectively, after the stopcock had been closed, limiting the volume to about 30 cc. At the end of the 20 minutes the light absorption of the O_2 was only 20 to 25 percent of its value at the beginning, i.e., from 75 to 80 percent of the O_2 molecules apparently had been "cleaned up." The discharge tube current for this run was 70 milliamperes, and plate exposure time 20 seconds for all seven spectrograms. To minimize the error resulting from the "photo-cleanup" effect on the O_2 pressure, the light was completely cut off from the absorption tube until just before an exposure was to be made, by drawing the solid end *f* (Fig. 2) of the diaphragm carrier in front of the lens, the larger volume (425 cc) of O_2 being always connected with the absorption chamber.

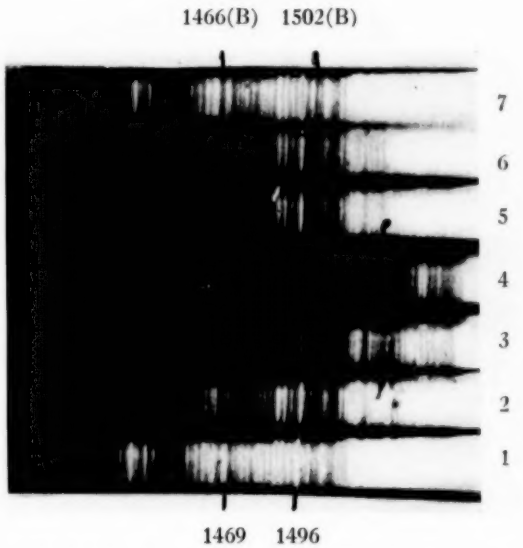

FIG. 3. Positives of spectrograms. Six and seven show the effect of clean up.

MEASUREMENT OF THE PLATES AND CALCULATION OF RESULTS

The absorption of O_2 was measured between 1670 and 1334A. The relative densities of the

[7] Cf. C. E. Kenneth Mees, J.O.S.A. **21**, 754 (1931).

lines (and of the continuous background[8]) of the several spectrograms on a plate were found by means of a photoelectric densitometer whose readings were rather accurately proportional to the transparency of the plate (which is of course not indispensable for the method used but rather useful) the reciprocals of the densitometer readings giving the relative densities.

For the calculations from the experimental data the absorption coefficient β was defined by the equation

$$I = I_0 e^{-\beta p l} \qquad (1)$$

where I_0 is the intensity of the light passing through the absorption tube when evacuated, I the light intensity after passing through a column of O_2 (in the absorption tube) of length l in cm and pressure p in cm (of Hg) at temperature 20°. For most of the spectrograms l was $=12.3$ cm though some measurements were made with the spectrograph filled with O_2, so that the light path for the wave-lengths investigated was nearly 3 times as large (34.5 cm). The β values calculated from these latter spectrograms agreed with the others within the errors of measurement. In order to correct for the effect of the part of continuous background on our plates because of scattered and fluorescence light in the spectrograph, the following graphical method was used to calculate the values of β for the different prominent hydrogen lines. For each line, logarithms of one thousand times (to make all logs positive in sign) the reciprocal of the densitometer scale readings in mm of the spectrograms taken with the absorption tube evacuated and the several diaphragms successively in position, were plotted as ordinates against the logarithms of the actual light intensities in percent, determined by the diaphragms, as abscissas. Then smooth curves were drawn through these points as shown in Fig. 4 for the examples λ1469 and λ1496 of the plate shown in Fig. 3, these lines having been chosen as illustrations, because the former is on this plate near the limit in weakness with which it was possible to make calculations while the latter is one of the very strongest lines. A small extrapolation of the curves when necessary can be done fairly accurately, because they must approach asymptotically the level marked "Clear Plate" in Fig. 4 which is determined by the densitometer readings in the dimmest parts of the spectrograms. From these plate-calibration curves the intensities of the light of these same wave-lengths after passing through some O_2 in the absorption chamber are found in the usual way. Also the apparent intensities of the light producing the continuous background of the plate is found in the same way from these curves and the densitometer readings of the clearer spaces between the lines of the plate. Thus, as shown in Fig. 4, with the absorption tube evacuated the intensity of the background, λ1466 (B) is 53.8 percent of the total intensity of λ1469 plus background, hence the true inten-

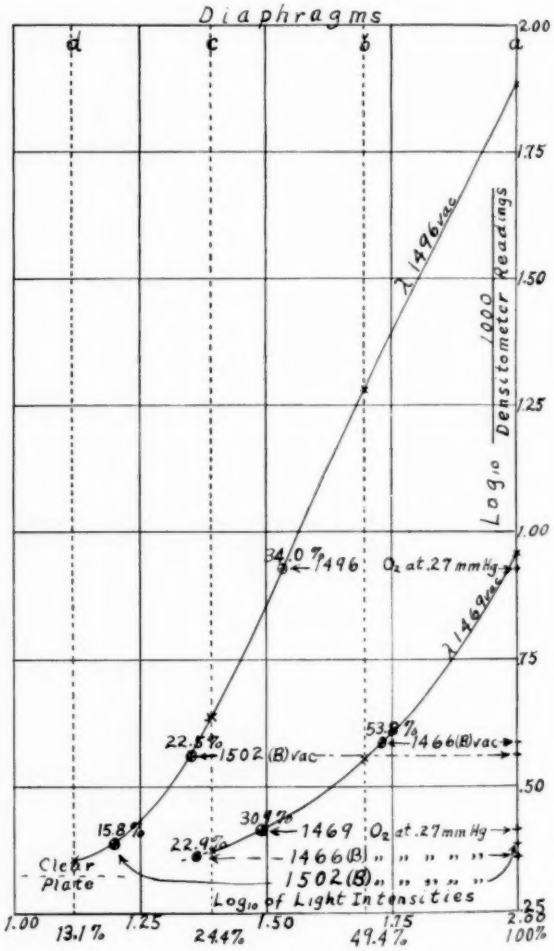

FIG. 4.

[8] In order to get good measurements the slit of the spectrograph had to be moderately wide, and on account of this, that part of the background which was produced by stray light of other wave-lengths was rather disturbing. This disturbance would be less if a spectrograph of wider dispersion were used.

sity of λ1469 alone is 46.2 percent of its apparent intensity. Likewise with 0.27 mm O_2 in the absorption tube, the apparent intensity of λ1469 is 30.9 percent of the apparent intensity without O_2, of which 22.9 percent is due to the background (the intensity of the light producing the background not being diminished by the same proportion as λ1469), hence the true value of the unabsorbed λ1469 is 30.9−22.9 or 8.0 percent, consequently $I=8.0/46.2=0.173$ or 17.3 percent of I_0, and therefore, for λ1469A

$$\beta=\left(\frac{2.30}{12.3}\right)\left(\frac{2-\log 17.3}{0.027}\right)=5.28.$$

For line 1496

$$I=(34.0-15.8)/(100-22.5)=0.235$$

or 23.5 percent of I_0, and

$$\beta=0.187(2-\log 23.5)/0.027=4.36.$$

Because of the disturbing influence of the background and the uncertainty of photographic-photometric measurements in this region of the spectrum we estimate that the error of the β values obtained may be as much as 5–10 percent.

Results and Discussion

The results are shown in the graph of Fig. 5 where we have drawn a smooth curve, although the measured values in the region of 6.6×10^4 seem to indicate a slight bend in the curve. Abscissas are wave numbers and the ordinates are absorption coefficients α which have been obtained by reducing the mean values of β mentioned in the last paragraph to N.P.T. of oxygen.

The absorption curve resembles a nearly symmetrically broadened spectral line with its maximum at $\nu=69{,}000$, $\lambda=1450$A, where the absorption is so strong that a layer of 0.0014 cm of O_2 at N.P.T. would reduce light of this wave-length to about one-half of its intensity. The absorbed light produces dissociation of the oxygen molecule into the atoms one of which is excited to the ^1D level. This action of the light is the cause for the clean up effect described above.

For $\lambda>1700$ and <1350A the absorption becomes very low—as a matter of fact our above-mentioned measurements with a large two meter grating spectrograph made in collaboration with Dr. J. C. Boyce have shown that between λ1300 and 1100 oxygen of 0.25 mm pressure is practically transparent in a layer of 4 m length. Above 1750A the line spectrum of the Schumann-Runge bands sets in, and we learn from our results that the absorption in these band lines is very much smaller than in the continuous part below 1700. This is just what one should expect from the application of the Franck-Condon principle to the potential energy curves of O_2 calculated by Morse[9] and Stueckelberg.[10] Recently Stueckelberg has shown[11] that it is even possible to calculate the distribution of the continuous absorption of O_2 from these potential energy curves following the way shown by Condon.[12] The thus calculated absorption curve is in fairly good agreement with our measurements.[13]

Finally we can compute the f value from the graph of the absorption coefficient by assuming

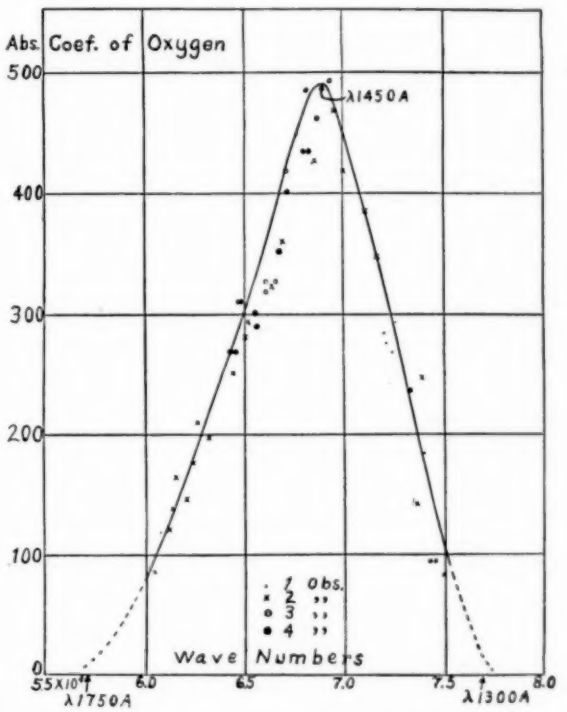

FIG. 5. Absorption coefficients of oxygen between 1750A and 1300A.

[9] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[10] E. C. G. Stueckelberg, Phys. Rev. **34**, 65 (1929).
[11] E. C. G. Stueckelberg, Phys. Rev. **42**, 518 (1932).
[12] E. U. Condon, Phys. Rev. **32**, 858 (1932).
[13] Compare Fig. 4 of Stueckelberg's second paper.

the classical relation between absorption and dispersion[14]

$$\int \alpha d\nu = \pi N f e^2/mc^2 = f \times 2.38 \cdot 10^7 \qquad (2)$$

where N means the number of molecules at N.P.T.[15] Thus we get for the absorption of oxygen in the Schumann region the value $f=0.193$ and $\lambda_{max}=1450$A in very good agreement with the conclusions drawn from the dispersion curve.[16]

Added in proof

On the other hand, since we know now the real distribution of absorption in the continuous part on the short wave-length side of the Schumann-Runge bands it seems worth while to calculate the influence of this continuous absorption upon the dispersion. For such calculations the following formula for the refractive index seems reasonable.

$$n(\nu)-1 = C\left[\Sigma_s \frac{f_s}{\nu_s^2-\nu^2} + \int \frac{\varphi(\omega)d\omega}{\omega^2-\nu^2}\right] \qquad (3)$$

where $C=Ne^2/2\pi mc^2$, the ν_s are resonance frequencies and f_s the corresponding "strengths." Now in analogy to the relation

$$\int \alpha d\omega = (\pi Ne^2/mc^2) f \quad \text{(compare Eq. (2))}$$

we may write

$$\alpha(\omega) = (\pi Ne^2/mc^2)\varphi(\omega),$$

so that Eq. (3) goes over into the equation[17]

$$n(\nu)-1 = C\Sigma_s \frac{f_s}{\nu_s^2-\nu^2} + \frac{1}{2\pi^2}\int \frac{\alpha(\omega)d\omega}{\omega^2-\nu^2}. \qquad (4)$$

This formula is obviously the reasonable generalization of a dispersion formula for a gas (outside its region of absorption) which shows a continuous absorption band besides its absorption lines —as every gas does.

The integral

$$G(\nu) \equiv \frac{1}{2\pi^2}\int_a^b \frac{\alpha(\omega)d\omega}{\omega^2-\nu^2}$$

between the limits $a=56{,}000$ and $b=78{,}000$ by using our values of α for oxygen given in the graph of Fig. 5 was kindly calculated for us by Mr. F. Seitz.[18] In the following Table I the

TABLE I. *Influence of the continuous absorption between 1750 and 1300A upon the dispersion of oxygen.*

ν	λ	$G(\nu)$ $\times 10^7$	$(n(\nu)-1)$ $\times 10^7$	$H(\nu)$ $\times 10^7$	$I(\nu)$ $\times 10^7$
55,000	1818A	1612			
52,084	1920	1277	3589	2312	2330
51,020	1960	1193	3508	2315	2323
50,000	2000	1125	3441	2316	2317
45,000	2222	907	3195	2288	2288
40,000	2500	768	3036	2268	2262
35,000	2860	680	2921	2241	2240
30,000	3333	618	2838	2220	2222
25,000	4000	573	2775	2202	2206

results for different values of ν between 55,000 and 25,000 ($\lambda=1818$ and 4000A) are given to as many places as the values of the dispersion of oxygen $(n(\nu)-1)$ measured by Ladenburg-Wolfsohn (L-W) which are also given in the table. The possible error of the G-values is at least ten times that of the dispersion values which are accurate to within one unit. If we try to represent the differences $n(\nu)-1-G(\nu)\equiv H(\nu)$ by one term $C\cdot f_s/\nu_s^2-\nu^2 \equiv I(\nu)$ (comp. Eq. (4)) we get the values $f_s=7.143$ and $\lambda_s=1/\nu_s=501.3$A instead of $f_3=5.928$ and $\lambda_3=544.4$A as was originally found by L-W who fitted the dispersion measurements by the usual formula with single resonance frequencies (compare p. 315). The agreement between the values $I(\nu)$ calculated in this way and the observed values $H(\nu)$ is quite good, considering the inaccuracy of the G-values and the fact that only two arbitrary constants f_s and ν_s are now used instead of four. The apparent systematic deviation at the highest frequencies ($\lambda=1960-1920$A, compare the table) can be explained by a slight change in the α-values within the errors of the absorption measurements.

[14] R. Ladenburg, Verh. d. D. Phys. Ges. **16**, 769 (1914); Zeits. f. Physik **4**, 451 (1921).

[15] The values used are: $N=2.706\times10^{19}$, $e=4.770\times10^{-10}$, $e/mc=1.76\times10^7$ and $c=2.998\times10^{10}$.

[16] It should be mentioned that from his measurements of the dispersion of air, J. Koch in 1912, had already deduced a resonance frequency of 1421A which he attributed to oxygen (Archiv. f. Math. Astr. och Fysik **8**, No. 20 (1912)). This paper was overlooked in the work of Ladenburg and Wolfsohn.[1]

[17] Compare the formula for the dispersion of Roentgen rays (H. Kallmann and H. Mark, Ann. d. Physik [4] **82**, 587 (1927) and other authors).

[18] We want to thank Mr. Seitz as well as Professor E. U. Condon for their valuable help in this matter.

This comparison shows further that not much weight can be put on the meaning of the resonance frequency ν_1 ($\lambda_1 = 1899$A) and the corresponding f-value $4.04 \cdot 10^{-5}$ as originally calculated from the dispersion measurements (compare p. 315). It is necessary to introduce this frequency as long as the dispersion measurements down to 1920A are represented by single resonance frequencies. But by taking into account the continuous absorption band it appears quite possible that the single weak lines of the Schumann-Runge bands have no appreciable influence upon the dispersion down to 1920A. But the absorption measurements are not accurate enough to decide this question.

The result of these considerations is that on the whole it is quite a good approximation to represent the dispersion measurements of molecular gases as oxygen by the usual dispersion formula using isolated resonance frequencies instead of taking care of the distribution of absorption in the absorption band, and when the dispersion measurements go near enough to the absorption band one gets in this way the position of the center of gravity of the absorption band and the value of $\int \alpha(\nu) d\nu$.

However a rigorous dispersion formula must be of the type of Eq. (4) which takes into account also the distribution of absorption in the continuous band.

The Spectra of the Calcium I-Like Ions: Manganese VI, Iron VII, Cobalt VIII and Nickel IX

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(Received December 9, 1932)

The spectra of four new ions have been added to the sequence of spectra isoelectronic with Ca I. A vacuum spark produced the radiation, which was analyzed in a vacuum spectrograph with a concave grating set for grazing incidence. The transitions observed were those between the ground configuration, $3d^2$, and the lowest configuration that combines with it, $3d\ 4p$. Nearly all the levels to be expected in these configurations were found, for all four spectra. Almost all the allowed transitions among the observed levels were identified, as were several intercombinations and other forbidden lines. Slater's theory for the levels (neglecting fine-structure) in a configuration gives a good fit with the observed multiplets, especially in $3d\ 4p$, which is remote from other odd configurations. In $3d^2$, $^1D_2$ is evidently perturbed by $3d\ 4s$.

THE observations here reported are an extension of those of Russell and Saunders[2] and Russell[3] on Ca I, Russell and Meggers[4] on Sc II, Russell and Lang[5] on Ti III, and White[6] on V IV and Cr V. This sequence of ions isoelectronic with Ca I is here extended so as to include the four new spectra: Mn VI, Fe VII, Co VIII and Ni IX, with a view to a comparison of the predictions of the theory of complex spectra with experimental results obtained with highly ionized atoms.

PART I. APPARATUS

The spectrograph was somewhat similar to that described by Hoag.[7] The light from a vacuum spark passed through the slit, and fell at a glancing angle of incidence upon the concave grating, whence it was diffracted and focussed on the curved photographic plate. The vacuum container was a brass tube, 93.6 cm in length by 20.4 cm in inner diameter. Therein rested a long base-plate, which carried the grating-mounting, plate-holder, and light-baffles; this base-plate was securely keyed in place, but could be removed for adjustment of the optical parts. The slit was carried by one of the two bronze castings that covered the ends of the tube.

A vacuum was produced in the spectrograph and in the glass spark-chamber by a Cenco Megavac pump, and maintained during exposures by a four-stage Leybold mercury diffusion pump (and traps cooled with solid CO_2), backed by a Cenco Hyvac pump.

The spark was excited by the discharge of a 0.33 μf capacity from a potential of 50,000 v. The discharge circuit was made as small as possible, in order to keep its inductance low, a condition which is necessary to high ionization in the source of light. A spark-gap in air, in series with the vacuum spark, was generally employed, since this seemed to improve the violence of the excitation. When it was desired to reduce the ionization, an inductance of about 0.02 mh was connected in series with the sparks.[8]

A new design for the slit was developed, which may merit description. For permanence of focus, it is essential that the position of the slit should not vary from one exposure to another. (This requirement is particularly important in grazing incidence spectrographs.) The frequent need of cleaning from the jaws the deposit of the spark necessitates a convenient way to replace the cleaned jaws accurately. This was accomplished by clipping one of the jaws (razor-blades) against

[1] National Research Fellow, at California Institute of Technology.

[2] Russell and Saunders, Astrophys. J. **61**, 38 (1925).

[3] Russell, Astrophys. J. **66**, 184 (1927).

[4] Russell and Meggers, Bur. Stand. Sci. Pap. **22**, No. 558 (1927).

[5] Russell and Lang, Astrophys. J. **66**, 13 (1927).

[6] White, Phys. Rev. **33**, 538 (1929).

[7] Hoag, Astrophys. J. **66**, 225 (1927).

[8] Gibbs, Vieweg and Gartlein, Phys. Rev. **34**, 406 (1929).

the flat vertical surface on which it rests, in such a way that its edge was tangent to two hardened steel pins, one above the other, which are set into that surface. The second jaw is shorter than the first, and is clipped in place between the pins so as to make the slit of the desired even width. The slit-width was usually about 0.02 mm.

The grating was ruled with 30,000 lines per inch on glass and etched by R. W. Wood; its radius of curvature was 197.9 cm. The glancing angle of incidence for which it was set was 6.3°, so that the dispersion at 200A was about one A/mm. Although the entire width (about 8 cm) of the grating was illuminated, ghosts were not in evidence except near the brightest lines.[9]

Schumann plates were used, as supplied by Hilger on very thin glass, 2×20 cm, which rarely broke when bent to the requisite radius of curvature of slightly less than a meter.

Part II. Procedure

With the pressure in the spark-chamber and spectrograph at about 10^{-4} mm Hg, the spark was started. The pressure thereupon rose to about 10^{-3} mm Hg, which pressure decreased slightly during the exposure, as the electrodes became outgassed. Since, therefore, the excitation does not at once come to its full violence, about the first twenty minutes were inefficient for the highest ionization; during this time, the inductance was placed in series with the spark. During the second twenty minutes, a different area of the plate was exposed, and the inductance was not in the circuit; lines that appeared with greatly increased intensity in the second exposure were thereby known to arise from highly ionized atoms[8]. One electrode was usually of aluminum, or aluminum cored with H_3BO_3, for the excitation of standard lines simultaneously with the unknown spectrum. Sometimes a third exposure was made, after a change of electrodes, of the standard spectrum only. Usually one or two seconds elapsed between sparks. The electrodes were not water cooled.

Between exposures on the same plate, a movable diaphragm, or occulter, before the plate, was lowered a fraction of an inch; the occulter was magnetically controlled from outside the spectrograph.

[9] Mack, Stehn and Edlén, J.O.S.A. **22**, 245 (1932).

The wave-lengths were determined by comparison with the spectrum of aluminum[10] and oxygen.[11] The interpolation was made quadratically on the wave-lengths among three standards, and a correction curve[12] constructed from the other neighboring standards. Neglecting ripples in the surface of the plate, the uncorrected quadratic interpolation should be, in the present case, valid to within 0.001A over a range of 30 mm.

Since the only line-group sought was that representing transitions between the $3d\ 4p$ and the $3d^2$ configurations, which are remote from each other, and compressed, the lines were, for each element, in a short section of the plate. The general position of the group for Mn VI could be predicted by extrapolation of the frequency of the same group as a function of the ionization along the Ca I-like sequence. When the Mn VI $3d^2-3d\ 4p$ lines were located, the position of those of Fe VII was predicted, and so on. The identification of the lines was facilitated by fairly accurate predictions of term separations, based on the centroid diagrams, Figs. 1 and 2.

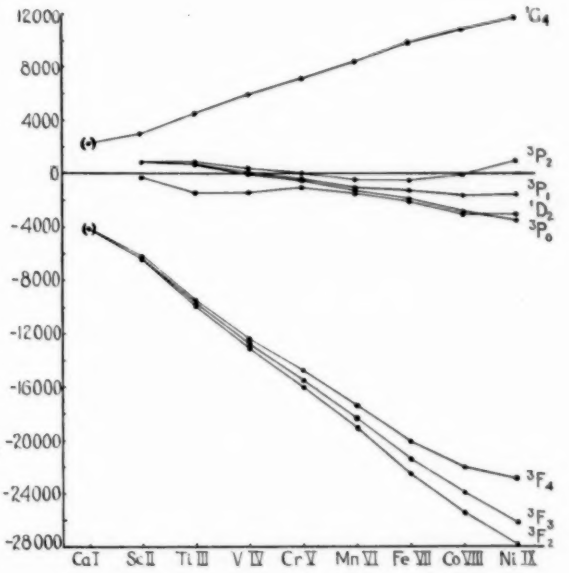

FIG. 1. Centroid diagram for $3d^2$.

[10] Söderquist and Edlén, Zeits. f. Physik **69**, 356 (1931).

[11] The writer is greatly indebted to Professor Siegbahn and to Mr. Edlén for permission to use an unpublished list of standards of oxygen, measured by Mr. Edlén at Upsala in 1931.

[12] Russell and Shenstone, J.O.S.A. **16**, 298 (1928).

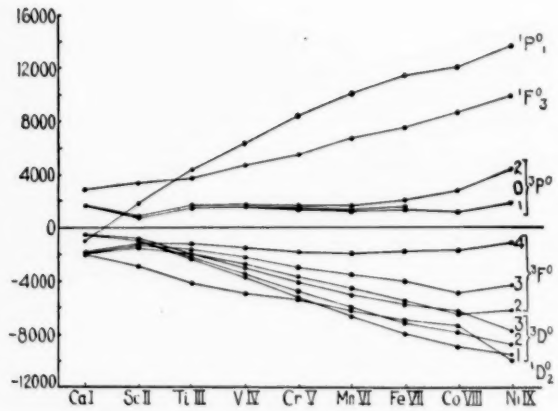

FIG. 2. Centroid diagram for $3d\,4p$.

The plates were rich in lines; no one group could ever be said to stand out as predominant. In the plates of Mn and Fe, however, the lines of Mn VI and Fe VII, respectively, were easy to pick out before the plates were measured; in these spectra about half of the lines in the ranges measured have been identified. In the Co and Ni plates, the groups under study were much fainter, and were somewhat obscured by a preponderance of lines from lower ionization. No line was ever specifically sought during the measurement of a plate.

PART III. RESULTS

In Tables I to IV the identified lines are recorded. The symbols sometimes following the estimated intensities in the first column have the significance: *n*, nebulous; *N*, very nebulous; *L*, present even when the inductance is in the spark circuit, as if the line is a blend with another line

TABLE I. *Lines of Mn VI.*

Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)	Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)
5	307.109	325617	$^3F_3-{}^3F_4^0$	3	9	320.681	311836	$^3P_0-{}^3P_1^0$	7
3	307.842	324842	$^3F_2-{}^3F_3^0$	1	9	320.874	311649	$^3P_1-{}^3P_0^0$?	0
20	307.999	324687	$^3F_4-{}^3F_4^0$	−4	9	320.979	311547	$^3P_1-{}^3P_1^0$	−15
20	308.560	324086	$^3F_3-{}^3F_3^0$	−1	11	321.176	311356	$^3P_2-{}^3P_2^0$	−2
15	308.853	323779	$^3F_3-{}^3F_2^0$	3	9	321.541	311002	$^3P_2-{}^3P_1^0$	1
12	309.440	323164	$^3F_4-{}^3F_3^0$	0	20	325.146	307554	$^1G_4-{}^1F_3^0$?	0
10	309.579	323019	$^3F_3-{}^3F_2^0$	−3	2	326.571	306212	$^1D_2-{}^3F_2^0$	39
10	310.058	322520	$^3F_3-{}^3D_3^0$	4				$^3P_2-{}^3F_3^0$	−28
9	310.182	322391	$^3F_2-{}^3D_2^0$	0	1*N*	327.131	305688	$^3P_1-{}^3F_2^0$	−48
40	310.908	321638	$^3F_2-{}^3D_1^0$	−53				$^1D_2-{}^3D_3^0$	21
			$^3F_3-{}^3D_2^0$	1	2	328.129	304758	$^1D_2-{}^3D_2^0$	−30
			$^3F_4-{}^3D_3^0$	45	10	328.232	304663	$^3P_2-{}^3D_3^0$	−6
10	311.748	320772	$^1D_2-{}^1P_1^0$	−15	20	328.431	304478	$^1D_2-{}^1D_2^0$	0
8	312.692	319804	$^3P_2-{}^1P_1^0$	15	9	328.558	304360	$^3P_1-{}^3D_2^0$	9
6	314.979	317481	$^1D_2-{}^1F_3^0$?	0	5	329.043	303912	$^3P_0-{}^3D_1^0$	−6
6	320.146	312357	$^1D_2-{}^3P_2^0$	1	2	329.177	303788	$^3P_2-{}^3D_2^0$	−2
9	320.598	311917	$^3P_1-{}^3P_2^0$	−2	5	329.320	303656	$^3P_1-{}^3D_1^0$	5

TABLE II. *Lines of Fe VII.*

Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)	Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)
6	231.047	432813	$^3F_3-{}^3F_4^0$	−22	4	236.501	422832	$^1D_2-{}^1F_3^0$?	0
5	231.641	431702	$^3F_2-{}^3F_3^0$	0	0*N*	239.605	417354	$^1D_2-{}^3P_2^0$	15
8	231.715	531564	$^3F_4-{}^3F_4^0$	13	8	240.075	416537	$^3P_1-{}^3P_2^0$	18
8	232.248	430574	$^3F_3-{}^3F_3^0$	−3	7	240.105	416484	$^3P_0-{}^3P_1^0$	37
6	232.432	430233	$^3F_2-{}^3F_2^0$	−14	1	240.370	416025	$^3P_1-{}^3P_0^0$?	9
2	232.579	429962	$^3F_2-{}^3D_3^0$	−5	1*n*	240.451	415886	$^3P_1-{}^3P_1^0$	9
3	232.945	429286	$^3F_4-{}^3F_3^0$	−7	5	240.563	415692	$^3P_2-{}^3P_2^0$	0
10	233.021	429146	$^3F_3-{}^3F_2^0$	24	1*N*	240.937	415047	$^3P_2-{}^3P_1^0$	−1
2*N*	233.187	428840	$^3F_3-{}^3D_3^0$	−2	50	243.375	410889	$^1G_4-{}^1F_3^0$?	0
8	233.309	428617	$^3F_2-{}^3D_2^0$	29	4	244.092	409682	$^3P_2-{}^3F_3^0$	23
8	233.703	427893	$^3F_2-{}^3D_1^0$	66	7	244.524	408958	$^3P_1-{}^3F_2^0$	−75
3	233.770	427771	$^3F_3-{}^1D_2^0$	16	4	244.803	408492	$^1D_2-{}^1D_2^0$	8
3	233.940	427460	$^3F_3-{}^3D_2^0$	−3	8	245.141	407928	$^3P_2-{}^3D_3^0$	4
			$^3F_4-{}^3D_3^0$	−98	7	245.481	407364	$^3P_1-{}^3D_2^0$	−10
9	234.339	426732	$^1D_2-{}^1P_1^0$	−22	3	245.596	407173	$^3P_0-{}^3D_1^0$	−10
15*B*?	234.779	425932	$^3P_1-{}^1P_1^0$?	−4	10	245.926	406626	$^3P_1-{}^3D_1^0$	13
10	235.232	425112	$^3P_2-{}^1P_1^0$	5	3	245.973	406549	$^3P_2-{}^3D_2^0$	4

TABLE III. *Lines of Co VIII.*

Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)	Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)
3*n*	181.994	549469	$^3F_3-{}^3F_4^0$	92	2	188.154	531480	$^3P_1-{}^3P_2^0$	−59
10*Ln*	182.665	547450	$^3F_2-{}^3F_3^0$	−178	2	188.232	531259	$^3P_0-{}^3P_1^0$	89
			$^3F_4-{}^3F_4^0$	−14	4*n*	188.673	530018	$^3P_1-{}^3P_1^0$	17
4*N*	183.125	546075	$^3F_3-{}^3F_3^0$	−32				$^3P_2-{}^3P_2^0$	39
			$^3F_2-{}^3F_2^0$	−27	4	189.249	528404	$^3P_2-{}^3P_1^0$	−37
3	183.542	544834	$^3F_3-{}^3D_3^0$	2	5	190.514	524896	$^1G_4-{}^1F_3^0$?	0
			$^3F_2-{}^3D_2^0$	41	2	190.843	523991	$^1D_2-{}^3D_3^0$	48
2	183.689	544398	$^3F_4-{}^3F_2^0$	204	1	190.954	523686	$^1D_2-{}^3F_2^0$	−6
4*n*	183.721	544304	$^3F_3-{}^3F_2^0$	−277	7*L*	191.247	522884	$^1D_2-{}^1D_2^0$	38
7	183.922	543709	$^3F_2-{}^3D_1^0$	22	3	191.465	522289	$^3P_1-{}^3F_2^0$	−38
3	183.941	543653	$^3F_2-{}^1D_2^0$	−82				$^3P_2-{}^3F_2^0$	−4
3*L*	184.053	543318	$^3F_3-{}^3D_2^0$	46	2	191.753	521504	$^3P_1-{}^1D_2^0$	23
70*B*	184.201	542885	$^3F_4-{}^3D_3^0$	−34				$^3P_0-{}^3D_1^0$	−39
3*LN*	184.421	542238	$^1D_2-{}^1P_1^0$	16	10*L*	191.923	521042	$^3P_1-{}^3D_2^0$	24
6	185.432	539281	$^3P_2-{}^1P_1^0$	−15				$^3P_2-{}^3D_3^0$	24
0	185.585	538837	$^1D_2-{}^1F_3^0$?	0	9*L*	192.328	519945	$^3P_1-{}^3D_1^0$	33
2	187.666	532862	$^1D_2-{}^3P_2^0$	−42	1	192.549	519348	$^3P_2-{}^3D_2^0$	−110

TABLE IV. *Lines of Ni IX.*

Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)	Int.	λ (A)	ν (obs.)	Transition	Δν (obs.-calc.)
6	146.068	684613	$^3F_3-{}^3F_4^0$	29	0	150.459	664633	$^3P_0-{}^3P_1^0$	−232
			$^3F_3-{}^3F_3^0$	−101	20	150.844	662938	$^3P_2-{}^3P_2^0$	−30
4	146.777	681305	$^3F_4-{}^3F_4^0$	29				$^3P_1-{}^3P_1^0$	0
			$^3F_2-{}^3F_2^0$	78	1	152.043	657709	$^1G_4-{}^1F_3^0$?	0
6	147.154	679560	$^3F_2-{}^3D_3^0$	−66	7	152.316	656531	$^1D_2-{}^3F_2^0$	29
			$^3F_3-{}^3F_2^0$	−21	0	152.700	654879	$^3P_1-{}^3F_2^0$	−113
0	147.370	678563	$^3F_2-{}^3D_2^0$	−66				$^1D_2-{}^3D_3^0$	−22
			$^3F_4-{}^3F_3^0$	−86	2*N*	152.859	654198	$^3P_2-{}^3F_2^0$?	−44
0	147.490	678012	$^3F_3-{}^3D_3^0$	32	6	152.975	653703	$^3P_0-{}^3D_1^0$	152
			$^3F_2-{}^3D_1^0$	153	1	153.212	652690	$^1D_2-{}^1D_2^0$	−8
0	147.861	676311	$^1D_2-{}^1P_1^0$	0	1	153.296	652333	$^3P_2-{}^3F_2^0$	−84
3	148.215	674697	$^3F_4-{}^3D_3^0$	25				$^3P_1-{}^3D_2^0$	−61
2*N*	148.688	672549	$^1D_2-{}^1F_3^0$?	0	1	153.645	650849	$^3P_2-{}^3D_3^0$	33
1	150.247	665572	$^3P_1-{}^3P_2^0$	29	12*B*?	154.174	648617	$^3P_2-{}^1D_2^0$?	4

of lower ionization; *B*, probably a blend with another line, of high ionization. The wave-lengths are, of course, for vacuum. The identifications, in the fourth column, are written with the final state first, followed by the initial state. The last column gives the difference between the term differences (as calculated from Tables V to VIII), and the observed frequencies.

Tables V to VIII give the term values. The symbol *E* following a term value signifies that the term has not been observed, but that its value has been estimated by extrapolation of the centroid diagram.

PART IV. DISCUSSION OF RESULTS

The random experimental errors can be estimated by the deviations Δν, column 5, Tables I to IV; actually the average of the deviations (regardless of sign) gives too low an estimate of the random errors, but it is of some value as a basis for the estimation of the latter. Table IX shows these errors.

The systematic errors cannot greatly affect the term separations within a configuration, and will not be considered; they arise mainly from the standards, of which the accuracy is probably between 0.01A and 0.03A.

All the known terms in $3d^2$ and $3d\,4p$ are set forth graphically in the centroid diagrams, Figs. 1 and 2. The terms are there plotted relatively to the parameter F_0 (which is the $I+F_0$ of Slater[13, 14]) for the respective configurations. This may be termed the true centroid of a configuration, since, in Slater's theory, it represents the

[13] Slater, Phys. Rev. **34**, 1293 (1929).

[14] Condon and Shortley, Phys. Rev. **37**, 1025 (1931).

TABLE V. *Terms of Mn VI.*

$3d^2$		$3d\,4p$	
$^3P_0$	17773	$^3P_0^0$	329689 ?
$^3P_1$	18040	$^3P_1^0$	329602
$^3P_2$	18601	$^3P_2^0$	329959
$^3F_2$	0	$^3D_1^0$	321691
$^3F_3$	754	$^3D_2^0$	322391
$^3F_4$	1677	$^3D_3^0$	323270
$^1S_0$		$^3F_2^0$	323776
$^1D_2$	17603	$^3F_3^0$	324841
$^1G_4$	27530 ?	$^3F_4^0$	326368
		$^1P_1^0$	338390
		$^1D_2^0$	322081
		$^1F_3^0$	335084 ?

TABLE VI. *Terms of Fe VII.*

$3d^2$		$3d\,4p$	
$^3P_0$	20644	$^3P_0^0$	437230 ?
$^3P_1$	21214	$^3P_1^0$	437091
$^3P_2$	22043	$^3P_2^0$	437735
$^3F_2$	0	$^3D_1^0$	427827
$^3F_3$	1125	$^3D_2^0$	428588
$^3F_4$	2409	$^3D_3^0$	429967
$^1S_0$		$^3F_2^0$	430247
$^1D_2$	20396	$^3F_3^0$	431702
$^1G_4$	32339 ?	$^3F_4^0$	433960
		$^1P_1^0$	447150
		$^1D_2^0$	428880
		$^1F_3^0$	443228 ?

TABLE VII. *Terms of Co VIII.*

$3d^2$		$3d\,4p$	
$^3P_0$	22606	$^3P_0^0$	554076 *E*
$^3P_1$	23775	$^3P_1^0$	553776
$^3P_2$	25335	$^3P_2^0$	555314
$^3F_2$	0	$^3D_1^0$	543687
$^3F_3$	1521	$^3D_2^0$	544793
$^3F_4$	3434	$^3D_3^0$	546353
$^1S_0$		$^3F_2^0$	546102
$^1D_2$	22410	$^3F_3^0$	547628
$^1G_4$	36351 ?	$^3F_4^0$	550898
		$^1P_1^0$	564632
		$^1D_2^0$	545256
		$^1F_3^0$	561247 ?

TABLE VIII. *Terms of Ni IX.*

$3d^2$		$3d\,4p$	
$^3P_0$	24308	$^3P_0^0$	689573 *E*
$^3P_1$	26235	$^3P_1^0$	689173
$^3P_2$	28810	$^3P_2^0$	691778
$^3F_2$	0	$^3D_1^0$	677859
$^3F_3$	1646	$^3D_2^0$	678629
$^3F_4$	4954	$^3D_3^0$	679626
$^1S_0$		$^3F_2^0$	681227
$^1D_2$	24725	$^3F_3^0$	683052
$^1G_4$	39565 ?	$^3F_4^0$	686230
		$^1P_1^0$	701036
		$^1D_2^0$	677423
		$^1F_3^0$	697274 ?

levels whence the several multiplets grow out. This definition of the centroid is particularly useful when a level is missing or strongly perturbed by another configuration.

The only theory of complex spectra which will be compared with the observed term schemes is that of Slater[13], which contemplates the inter-multiplet separations within a configuration, neglecting the effect of fine-structure and of perturbations between configurations. Condon and Shortley[14] have applied this theory to several cases where the observations were sufficiently complete; the data presented here provide eight new configurations in which to test the theory.

Slater's theory predicts that in a d^2 configuration which is remote from other even configurations, and in which the fine-structure separations are much less than the distances between multiplets, the frequencies of the multiplets are given by

$$^1S = F_0 + 14F_2 + 126F_4 \qquad ^3F = F_0 - 8F_2 - 9F_4$$

$$^3P = F_0 + 7F_2 - 84F_4 \qquad ^1G = F_0 + 4F_2 + F_4$$

$$^1D = F_0 - 3F_2 + 36F_4$$

where the F's are, effectively, parameters to be adjusted to fit the data. Further, another set of parameters, F_0, F_2, G_1 and G_3, should exist, such that, in a configuration $d \cdot p$, subject to the restrictions that the multiplets are narrow and that no other odd configurations are near,

$$^1P^0 = F_0 + 7F_2 + G_1 + 63G_3$$

$$^3P^0 = F_0 + 7F_2 - G_1 - 63G_3$$

$$^1D^0 = F_0 - 7F_2 - 3G_1 + 21G_3$$

$$^3D^0 = F_0 - 7F_2 + 3G_1 - 21G_3^0$$

$$^1F^0 = F_0 + 2F_2 + 6G_1 + 3G_3$$

$$^3F^0 = F_0 + 2F_2 - 6G_1 - 3G_3.$$

By way of definition, the observed frequency of a multiplet is taken as the average of its fine-structure components, weighted according to their values of $2J+1$. This frequency may be called the centroid of a multiplet; it represents the position from which the fine-structure terms spread out.[15] As is to be expected, the above

[15] See, for instance, Houston, Phys. Rev. 33, 297 (1929).

TABLE IX.

	Mn VI	Fe VII	Co VIII	Ni IX
Ave. $\lvert\Delta\nu\rvert$ (cm^{-1})	11	16	47	55
Ave. $\lvert\Delta\lambda\rvert$ (A)	0.011	0.009	0.017	0.013

definition allows a somewhat better fit of the above formulas than does an unweighted mean of the terms for each multiplet.

In $3d^2$, ^1S is not known,[14] and ^1D is (except in Sc II) depressed by $3d\ 4s\ ^1D$, ^3D, of the same parity, which lies above it. Therefore we calculate the F's for $3d^2$ from the three other levels: ^3P, ^3F, and ^1G. With the parameters so determined, we compute ^1D, and compare the observed value with the one so computed. The result is in the sense of an observed depression of ^1D, except in the case of Sc II, where $3d\ 4s$ lies below $3d^2$. The possibility of a perturbation between $3d^2$, $^3P_2$ and $^1D_2$ is here neglected.

Table X shows the values of the F's for $3d^2$, and also the perturbation $p = {}^1D_{\text{obs.}} - {}^1D_{\text{calc.}}$. For reference, there is also tabulated the frequency difference f = (centroid of $3d\ 4s$) − (centroid of $3d^2$), and p/Z_0, where Z_0 is the Roman numeral of the spectrum. The figures in parentheses are estimated by extrapolating from known data.[4, 5, 6]

TABLE X.

	Sc II	Ti III	V IV	Cr V	Mn VI	Fe VII	Co VIII	Ni IX
F_0	11263	9874	13141	16056	19098	22521	25438	27836
F_2	736.8	1110.4	1456	1758	2062	2402	2670	2871
F_4	51.11	83.16	119.0	148.8	181.1	211.0	233.5	243.9
p	52	−1065	−1397	−1219	−1827	−2516	−3424	−3277
f	−9939	30116	85583	154242	(250000)	(360000)	(490000)	(630000)
p/Z_0	26	−355	−349	−244	−304	−359	−428	−364

TABLE XI.

	Ca I	Sc II	Ti III	V IV	Cr V	Mn VI	Fe VII	Co VIII	Ni IX
F_0	37698	28966	79404	149903	233226	328317	435718	552606	687369
F_2	78	242	444	583	709	841	955	1032	1276
G_1	366	380	435	534	616	730	796	902	1002
G_3	−24.0	2.7	15.2	30.2	47.4	60.1	69.0	71.5	70.8
Δ^1P^0	−366	−394	−109	−165	−167	−330	−396	−604	−727
Δ^3P^0	−52	−323	−133	−43	143	122	204	240	−174
Δ^1D^0	286	−108	−113	120	435	579	786	1078	505
Δ^3D^0	−524	−290	−28	−228	−445	−697	−893	−1286	−1016
Δ^1F^0	560	607	169	254	258	525	617	951	1129
Δ^3F^0	101	505	210	70	−227	−197	−322	−378	283
Acc.	6.7%	5.9%	1.5%	1.3%	2.0%	2.5%	2.9%	3.9%	2.7%

It is to be noted that p/Z_0 is roughly constant, except for Sc II.

Table XI gives the best (least square) values of the F's and G's for $3d\ 4p$, and the discrepancy (observed − calculated) for each multiplet. As before, F_0 is tabulated relatively to the ground state, for each spectrum. The last row gives the average discrepancy (regardless of the sign of the individual discrepancies), divided by the over-all width of the configuration. The theory is not, however, quite as successful as is indicated by this measure of its accuracy; the parameters could be adjusted to fit any six arbitrarily chosen numbers, with an "accuracy" of better than 50 percent.

The observed departures from theory in $3d\ 4p$ probably arise mainly from magnetic perturbations (between terms of like J), which were not contemplated by Slater. The predictions of Johnson[16] could be tested here, but this has not been undertaken.

The unobserved configuration $4s\ 4p$ is about as close to $3d\ 4p$ as $3d\ 4s$ is to $3d^2$, since the difference is, in both cases, that between a $3d$ and a $4s$ electron. Perhaps, then, the inaccuracy of the theory in $3d\ 4p$ is partly to be referred to a perturbation by $4s\ 4p$, $^1P^0$ and $^3P^0$. The apparent absence of any large perturbation of this sort can

[16] Johnson, Phys. Rev. **38**, 1628 (1931).

perhaps be construed as evidence against the correctness of the above discussion of $3d^2$.

In the centroid diagram for $3d\ 4p$, Fig. 2, we observe that $^3D^0$ and $^3F^0$ lie very close together. This results in a confusion of identity between $^3D_2^0$ and $^3F_2^0$, and between $^3D_3^0$ and $^3F_3^0$; forbidden lines $^3P-{}^3F^0$ appear, since ^3P combines with $^3D^0$. The L-values of the four mixed levels might have been assigned oppositely, with equal justification. Many intercombination lines appear between the singlet and triplet systems, further evidence that we are dealing with coupling that is not strictly LS. The partial inversion of $^3P^0$ probably arises from a perturbation between $^1P_1^0$ and $^3P_1^0$, in the sense of a depression of the latter to a point below $^3P_0^0$; in Ca I, however, $^3P^0$ is normal, because $^1P^0$ is here below $^3P^0$.

It is with great pleasure that I acknowledge my debt to Professor Lyman of Harvard University, under whose guidance all the experimental part of this research was done, and to Professor Houston of the California Institute of Technology, for his valuable suggestions as to the preparation of Part IV.

Quantum Mechanics of Beryllium Hydride

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The interaction of a normal hydrogen atom with a beryllium atom having the electronic configurations $2s\ 2s$ and $2s\ 2p$, respectively, has been studied by the application of a modified Heitler-London method. It is shown that for beryllium in the ^1S atomic state, the resulting $^2\Sigma$ molecular state is repulsive. For beryllium in the ^3P atomic state, the $^4\Pi$ and $^4\Sigma$ molecular states are repulsive, and the $^2\Pi$ and $^2\Sigma$ states are attractive. For beryllium in the ^1P atomic state both the $^2\Pi$ and $^2\Sigma$ molecular states are found to be repulsive. However, when the interaction between the $^2\Sigma(^3P+^3S)$ and the $^2\Sigma(^1S+^3S)$ molecular states is taken into account the lowest $^2\Sigma$ state is found to be attractive. The calculated heats of dissociation for the attractive states are in poor agreement with the extrapolated values from the band system.

INTRODUCTION

IN a recent series of papers,[1, 2, 3, 4] the Heitler-London method has been developed and applied to a study of the lithium and beryllium molecules. The results have not been encouraging, but before resorting to more elaborate and complicated methods of calculation, it seems to the point to ascertain whether or not the method, despite its limitations and imperfections, can be used with some success in other cases. If, in particular, one could arrive at a qualitative understanding of the formation of the hydrides, this would be at least a step toward a more perfect theory of valence. Hutchisson and Muskat[5] have made a beginning by calculating the heat of dissociation of lithium hydride. They found good agreement with the experimental value.

The purpose of the present paper is to study the next more complicated hydride, namely, beryllium hydride. The Heitler-London method has been applied to those states of BeH which dissociate into a normal hydrogen atom, and a beryllium atom in the ^1S, ^3P and ^1P atomic states, respectively.

The atomic wave functions used are similar to those given by Zener[6] except that the coefficient in the exponent in the case of Be has been raised from 0.96 to unity. It has been shown[4] that the integrals arising in a calculation of this type are quite insensitive to small changes in the coefficient in the exponent, and this has been verified for a number of the integrals occurring in the present case. This change is made because of the great simplification which results in the calculation, since the tables of the previous papers[1, 3] can be used.

NOTATION

The normalized atomic wave function for electron 1, on the beryllium nucleus, with quantum numbers (n, l, m) will be denoted by $a(n, l, m/1)$; similarly for hydrogen, $b(n, l, m/1)$. For simplicity $a(2, 0, 0/1)$ will be written $a(s/1)$; $b(1, 0, 0/1)$ will be written $b(1)$; and both $a(2, 1, 0/1)$ and $a(2, 1, 1/1)$ will be written $a(p/1)$. Thus in the latter case the general formulation will hold for either Π or Σ states depending upon the value of m. The atomic wave functions are:

$$b(1)=\pi^{-\frac{1}{2}}e^{-b_1};\quad a(s/1)=(3\pi)^{-\frac{1}{2}}a_1e^{-a_1},$$

$$a(p/1)=\pi^{-\frac{1}{2}}a_1\cos\theta_{a_1}e^{-a_1}\text{ for }m=0,$$

$$a(p/1)=(2\pi)^{-\frac{1}{2}}a_1\sin\theta_{a_1}e^{i\phi_1-a_1}\text{ for }m=1.$$

Let

$$S^1=\int a(s/1)b(1)dv,$$

$$S^1(p)=\int a(p/1)b(1)dv,$$

[1] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).

[2] J. H. Bartlett, Jr., and W. H. Furry, Phys. Rev. **38**, 1615 (1931).

[3] W. H. Furry and J. H. Bartlett, Jr., Phys. Rev. **39**, 210 (1932).

[4] W. H. Furry, Phys. Rev. **39**, 1015 (1932).

[5] E. Hutchisson and M. Muskat, Phys. Rev. **40**, 340 (1932).

[6] Clarence Zener, Phys. Rev. **36**, 51 (1930).

$$J(s,s;b,b)=\int[a(s/1)]^2H'(13)[b(3)]^2dv,$$

$$K(s,b;s,b)=\int a(s/1)b(1)H'(13)a(s/3)b(3)dv,$$

$$J''(s,s;s,b)=\int[a(s/1)]^2H'(13)a(s/3)b(3)dv,$$

$$J''(s,b;s,p^*)=\int a(s/1)b(1)H'(13)\times a(s/3)a^*(p/3)dv.$$

The above examples are sufficient for the understanding of further integrals. All energies are to be measured relative to the energy of the separate atoms at infinite separation. Atomic units are used unless otherwise stated. A complete tabulation of integrals is given in the appendix.

I. Interaction of Normal Hydrogen with Normal Beryllium

Assume the following as a suitable normalized molecular wave function:

$$\psi_a=[6(1-S)]^{-\frac{1}{2}}\sum_P(-1)^{\sigma_P}P[a_\alpha(s/1)a_\beta(s/2)b_\alpha(3)].$$

The total energy is given by

$$E=\int\psi_a^*H\psi_a dv.$$

Splitting off the unperturbed energy, say E_0, and substituting for ψ_a, results in

$$E-E_0=E'=[6(1-S)]^{-1}\int\left[\sum_P(-1)^{\sigma_P}Pa_\alpha(s/1)a_\beta(s/2)b_\alpha(3)\right]H'\cdot\left[\sum_P(-1)^{\sigma_P}Pa_\alpha(s/1)a_\beta(s/2)b_\alpha(3)\right]dv,$$

where the perturbative part of the Hamiltonian is

$$H'=H'(13)+H'(23)$$

and

$$H'(i3)=2/R+2/r_{i3}-2/a_3-2/b_i.$$

Suppressing P in the second bracketed expression in the integral introduces a factor of 6. The perturbative part of the energy is

$$E'=\frac{2J(s,s;b,b)-K(s,b;s,b)-S^{\frac{1}{2}}J''(s,s;s,b)}{(1-S)}.$$

Table I gives the energy of the $^2\Sigma(^1S+^2S)$ state as a function of the internuclear distance R.

Table I. *Energy of the* $^2\Sigma(^1S+^2S)$ *state.*

R	$S^{\frac{1}{2}}$	$J(s,s;b,b)$	$K(s,b;s,b)$	$J''(s,s;s,b)$	E'
2.0	0.66801	−0.02427	−0.1984	−0.06526	0.349
2.5	0.57300	−0.03356	−0.1677	−0.07837	0.217
3.0	0.47704	−0.02549	−0.1172	−0.06617	0.126
4.0	0.30490	-0.0^23290	−0.04219	−0.03230	0.05012
5.0	0.18089	-0.0^21648	−0.01256	−0.01338	0.01208

II. The Excited States

One may write the following eight molecular wave functions, the first six arising from the ^3P atomic state of beryllium and the last two from the ^1P atomic state. Thus

$$\psi_1=0\{(\varphi_1-\varphi_2)b(3)\alpha(1)\alpha(2)\alpha(3)\},$$

$$\psi_2=0\{(\varphi_1-\varphi_2)b(3)\alpha(1)\alpha(2)\beta(3)\},$$

$$\psi_3=0\{(\varphi_1-\varphi_2)b(3)[\alpha(1)\beta(2)\alpha(3)+\alpha(2)\beta(1)\alpha(3)]\},$$

$$\psi_4=0\{\varphi_1-\varphi_2)b(3)[\alpha(1)\beta(2)\beta(3)+\alpha(2)\beta(1)\beta(3)]\},$$

$$\psi_5=0\{(\varphi_1-\varphi_2)b(3)\beta(1)\beta(2)\alpha(3)\},$$

$$\psi_6=0\{(\varphi_1-\varphi_2)b(3)\beta(1)\beta(2)\beta(3)\},$$

$$\psi_7=0\{(\varphi_1+\varphi_2)b(3)[\alpha(1)\beta(2)\alpha(3)-\alpha(2)\beta(1)\alpha(3)]\},$$

$$\psi_8=0\{(\varphi_1+\varphi_2)b(3)[\alpha(1)\beta(2)\beta(3)-\alpha(2)\beta(1)\beta(3)]\},$$

where 0 stands for the operator $\sum_p (-1)^{\circ_P} P$ and

$$\varphi_1 = a(s/1)a(p/2); \quad \varphi_2 = a(s/2)a(p/1).$$

In order to get a molecular wave function which will give rise to $^2\Pi$ or $^2\Sigma$ states and whose atomic states are ^3P for beryllium and ^2S for hydrogen one will have to take a linear combination of the functions ψ_2 and ψ_3, thus $\psi_b = C_2\psi_2 + C_3\psi_3$. The secular equation may be written as follows:

$$\begin{vmatrix} H_{22}-E & H_{23}-FE \\ H_{32}-FE & H_{33}-E \end{vmatrix} = 0,$$

where

$$H_{ij} = \frac{\int \psi_i^* H \psi_j dv}{[\int |\psi_i|^2 dv \cdot \int |\psi_j|^2 dv]^{\frac{1}{2}}} = H_{ji}$$

and $F = H_{ij}$ for $H = 1$ and $(ij) = (23)$. The energies for both the doublet and quartet states are obtained from the secular equation, and a check can be made by solving for the energy of the quartet states directly by using ψ_1 as the molecular wave function. Thus

$$(E - E_0) = \int \psi_1^* H' \psi_1 dv \Big/ \int \psi_1^* \psi_1 dv = H_{11}'.$$

The evaluation of the H''s offers no difficulty, and so they will merely be listed:

$$H_{11}' = \{J(s,s;b,b) - K(s,b;s,b) - K(p,b;p^*,b) - S^{\frac{1}{2}}(p)[J''(s,s;p^*,b) - J''(s,p^*;s,b)] + S^{\frac{1}{2}}[J''(p,s;p^*,b) - J''(p^*,p;s,b)]\} \div [1 - S - S(p)],$$

$$H_{22}' = J(s,s;b,b) + J(p^*,p;b,b),$$

$$H_{33}' = \{2J(s,s;b,b) + 2J(p^*,p;b,b) - K(s,b;s,b) - K(p,b;p^*,b) - S^{\frac{1}{2}}(p)[J''(s,s;p^*,b) - J''(s,p^*;s,b)] + S^{\frac{1}{2}}[J''(p,s;p^*,b) - J''(p^*,p;s,b)]\} \div [2 - S - S(p)],$$

$$H_{23}' = \{-K(s,b;s,b) - K(p,b;p^*,b) - S^{\frac{1}{2}}(p)[J''(s,s;p^*,b) - J''(s,p^*;s,b)] + S^{\frac{1}{2}}[J''(p,s;p^*,b) - J''(p^*,p;s,b)]\} \div [2 - S - S(p)]^{\frac{1}{2}}.$$

Also

$$F = -[S + S(p)][2 - S - S(p)]^{-\frac{1}{2}}.$$

The integrals are of the types dealt with in the previous papers.[1-3]

Table II gives the energies of the $^2\Sigma(^3P + ^2S)$ and $^4\Sigma(^3P + ^2S)$ states, together with the values of new integrals arising in this connection and the values of the constants C_2 and C_3 (see Part III). Table III gives the corresponding information for the Π-states.

TABLE II. *Energies of the* $^2\Sigma$ *and* $^4\Sigma$ $(^3P + ^2S)$ *states.*

R	2.0	2.5	3.0	4.0	5.0
$J(p^*p;bb)$	−0.08727	−0.07125	−0.05172	−0.01312	-0.0^2462
$K(pb;p^*b)$	−0.1562	−0.1641	−0.1332	−0.06128	−0.02060
$J''(ps;p^*b)$	−0.03242	−0.02005	-0.0^2748	+0.01580	+0.02021
$J''(p^*p;sb)$	−0.1504	−0.1444	−0.1114	−0.07639	+0.04590
$J''(ss;pb)$	−0.01816	−0.05648	−0.06420	−0.06176	−0.04276
$J''(sp^*;sb)$	−0.06607	−0.02586	-0.0^279	+0.01830	+0.01062
$S^{\frac{1}{2}}(p)$	0.58645	0.57288	0.52276	0.37851	0.24145
H_{22}'	−0.1115	−0.1048	−0.0772	−0.01641	-0.0^2627
H_{22}'	0.3685	0.3628	0.2721	0.1219	0.02996
H_{33}'	0.1506	0.1570	0.1192	0.07319	0.01512
$E'(^2\Sigma)$	−0.2252	−0.2372	−0.1950	−0.08705	−0.02580
$H_{11}'(^4\Sigma)$	1.400	0.9191	0.5128	0.1904	0.03864
C_2	0.6912	0.7085	0.7304	0.7723	0.7982
C_3	−0.3801	−0.4105	−0.4470	−0.5128	−0.5516

TABLE III. *Energies of the* $^2\Pi$ *and* $^4\Pi(^3P + ^2S)$ *states.*

R	2.0	2.5	3.0
$J(p^*,p;b,b)$	0.02518	0.0^2258	-0.0^2188
$K(p,b;p^*,b)$	0.05448	0.03427	0.02001
$J''(p,s;p^*,b)$	0.08316	0.06154	0.04517
$J''(p^*,p;s,b)$	-0.0^264	−0.0432	−0.0442
H_{22}'	0.0^2916	−0.03098	−0.02737
H_{23}'	0.1634	0.1496	0.1050
H_{33}'	0.1323	0.07866	0.04879
$E'(^2\Pi)$	−0.0825	−0.1097	−0.0871
$H'_{11}(^4\Pi)$	0.3695	0.2419	0.1461

The energy arising from the interaction of a beryllium atom in the ^1P atomic state and a hydrogen atom in the normal state is given by:

$$H_{77}' = \int \psi_7^* H' \psi_7 dv \Big/ \int \psi_7^* \psi_7 dv = \{2J(s,s;b,b) + 2J(p^*,p;b,b) - K(s,b;s,b) - K(p,b;p^*,b)$$
$$- S^{\frac{1}{2}}(p)[J''(s,s;p^*,b) + J''(s,p^*;s,b)] - S^{\frac{1}{2}}[J''(p,s;p^*,b) + J''(p^*,p;s,b)]\} \div [2 - S - S(p)].$$

The energies are listed in Table IV.

TABLE IV. *Energies of interaction between Be(^1P) and normal hydrogen.*

R	2.0	2.5	3.0	4.0	5.0
$E'(^2\Sigma)$	0.2504	0.1962	0.1245	0.05987	$0.0^2 8601$
$E'(^2\Pi)$	0.06083	0.03646	0.02448	——	——

III. The Ground State*

Since the potential energy curve (see Fig. 1) for the $^2\Sigma(^3P + ^2S)$ molecular state crosses that of the $^2\Sigma(^1S + ^2S)$ state one would expect a considerable perturbing effect between these two states, and so as a suitable wave function for a ground state one assumes $\psi = C_a\psi_a + C_b\psi_b$. The constants C_2 and C_3 in ψ_b may be evaluated readily by first getting their ratio by using the H''s and $E'(^2\Sigma)$ in Table II, and then applying the normalization condition to ψ_b. The values so obtained are given in Table II. Now if one measures the energy of the ground state relative to the ^1S level of beryllium, and lets $\epsilon(=0.2008)$ denote the energy difference between the ^1S and ^3P levels one may write the secular equation for the ground state as follows:

$$\begin{vmatrix} H_{aa}' - E & H_{ab}' - \bar{F}(E-\epsilon) \\ H_{ba}' - \bar{F}E & H_{bb}' - (E-\epsilon) \end{vmatrix} = 0,$$

where $H_{ij}' = \int \psi_i^* H' \psi_j dv$, and $\bar{F} = \int \psi_a^* \psi_b dv$.

Clearly, H_{aa}' is the energy of the $^2\Sigma(^1S + ^2S)$ state relative to the ^1S atomic level and H_{bb}' is the energy of the $^2\Sigma(^3P + ^2S)$ state relative to the ^3P atomic level. The evaluation of H_{ab}' is rather laborious for in this case the permutations on both ψ_a and ψ_b must be carried out since the quantum numbers are not the same on both functions. The evaluation gives

$$H_{ab}' = \tfrac{1}{3}(1-S)^{-\frac{1}{2}}[C_2 - C_3/w^{\frac{1}{2}}]\{S^{\frac{1}{2}}[2J''(s,p^*;s,b) - J''(s,s;p^*,b) + 2J''(s,b;s,p) - J''(p,b;s,s)]$$
$$- S^{\frac{1}{2}}(p)[J''(s,s;s,b) + J''(s,b,s,s)] - K(s,b;p,b) - K(p,b;s,b)\}.$$

Also

$$\bar{F} = -(1-S)^{-\frac{1}{2}}[C_2 - C_3/w^{\frac{1}{2}}]S^{\frac{1}{2}}S^{\frac{1}{2}}(p),$$

where $w^{\frac{1}{2}} = [2 - S - S(p)]^{\frac{1}{2}}$.

In Table V are listed the values of new integrals occurring in the calculation of the ground state together with the values of the energy E' of this state. E'' represents the energy of the higher $^2\Sigma$ molecular state which results from the perturbation in question. The energies E' are measured from the dissociated state $^3P + ^2S$ while the energies E'' relate to the dissociated state $^1S + ^2S$.

* As a further example of the perturbing effects of adjacent states see W. H. Furry's letter to the editor in this issue.

TABLE V. $^2\Sigma$ (*ground state*).

R	$K(s,b;p,b)$	$J''(s,b;s,s)$	$K(p,b;s,b)$	$J''(s,b;s,p)$	$J''(p,b;s,s)$	H_{ab}'	$\bar{F}$	E'	E''
2.0	−0.0937	−0.4132	−0.3278	0.1600	−0.6741	+0.5989	−0.5457	−0.200	+1.307
2.5	−0.1091	−0.4478	−0.2662	0.1445	−0.6999	+0.5387	−0.4254	−0.255	+0.789
3.0	−0.0986	−0.4219	−0.1954	0.1182	−0.6570	+0.4174	−0.3102	−0.230	+0.441
4.0	−0.04077	−0.2998	−0.07254	0.06924	−0.4980	+0.1876	−0.1403	−0.0825	+0.0985
5.0	−0.01392	−0.1870	−0.02264	0.03107	−0.3227	+0.06739	−0.05316	-0.0^2845	+0.0018

IV. Discussion

The analysis of the band systems of beryllium hydride[7] shows that the electronic transition in question is $^2\Pi$ to $^2\Sigma$ indicating that the normal state is $^2\Sigma$, dissociating into beryllium in the ^1S state and hydrogen in the ^2S state. Now it is to be observed from the potential energy curves for earth-alkali hydrides given by Mulliken[8] that, as the separation between the ground state and the first excited state increases, the ground state becomes less attractive. For HgH, the ground state is almost repulsive.

The calculation in Part I shows that a normal beryllium atom and a normal hydrogen atom will combine to give a repulsive molecular state. Mercury hydride would probably be similar, so that the theory seems to check the experimental results here. Accordingly, the reason that the ground state of BeH is, in fact, attractive, must be that the higher $^2\Sigma$ states exert a considerable influence. This is verified by the calculation in Part III.

The calculation in Part II shows that a normal hydrogen atom and a beryllium atom in the ^3P atomic state will combine to give an attractive $^2\Pi$ state and to this approximation, an attractive $^2\Sigma$ molecular state, and repulsive $^4\Pi$ and $^4\Sigma$ molecular states. The equilibrium distance is about the same for the attractive states, but the heat of dissociation of the $^2\Sigma$ molecular state is about twice as great as that for the $^2\Pi$ state. This is of no immediate physical interest, because of the perturbing effect of the nearby $^2\Sigma$ state, but it may be helpful in the construction of a more complete theory of "directed" valence. One should note, however, that, of the states arising from ^1P and ^2S, the $^2\Pi$ is the lower.

For the ground state and the first excited state the following molecular constants have been calculated: (the numbers in brackets refer to the work of Olsson[7])

State	Internuclear distance (Angstroms)	Heat of dissociation (electron-volts per molecule)
$^2\Sigma$	1.37 [1.34]	3.5 [2.13]
$^2\Pi$	1.35 [1.33]	1.5 [2.22]

It is further seen from Fig. 1 that the $^2\Sigma$ state arising from the interaction of a normal hydrogen atom with a $2s\,2p\,^1P$ beryllium atom is repulsive, which would indicate that the effect of spin valency is more important than that of orbital valency. It is not certain whether the $^2\Pi$ state arising from this configuration is repulsive or slightly attractive at larger internuclear distances than calculated.

In conclusion, the writer wishes to express his indebtedness to Professor J. H. Bartlett, Jr. for suggesting the problem and for his constant interest. Thanks are also due to Dr. W. H. Furry for the use of certain unpublished tables.

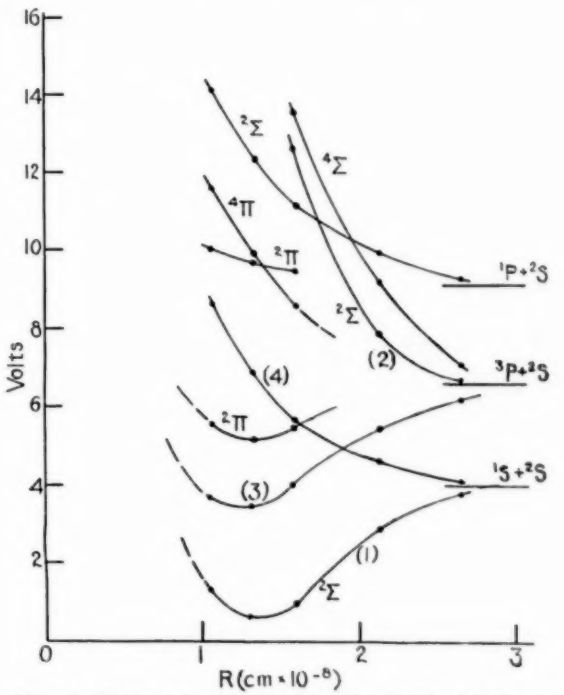

FIG. 1. Potential energy curves for BeH. (1) Ground state, resulting from perturbing effect of the $^2\Sigma(^1S+^2S)$ state on the $^2\Sigma(^3P+^2S)$ state. (2) $^2\Sigma(^1S+^2S)$ state after being perturbed by the $^2\Sigma(^3P+^2S)$ state. (3) $^2\Sigma(^3P+^2S)$ state, neglecting perturbation by other states. (4) $^2\Sigma(^1S+^2S)$ state, neglecting perturbation by other states.

[7] Ernst Olsson, Zeits. f. Physik **73**, 732 (1932).
[8] R. S. Mulliken, Rev. Mod. Phys. **4**, 8 (1932).

Appendix: Tabulation of Integrals

I. Σ states

$$S^{\frac{1}{2}}=[R^4/4(3)^{\frac{1}{2}}][A_3(1,R)-\tfrac{1}{3}A_1(1,R)],$$

$$S^{\frac{1}{2}}(p)=(3^{\frac{1}{2}}R/4)I_b(sb),$$

$$I_b(sb)=(R^3/3^{\frac{1}{2}})[A_2(1,R)-\tfrac{1}{3}A_0(1,R)],$$

$$I_b(bb)=8R^2[A_2(0,2R)-A_2(1,2R)],$$

$$I_a(ss)=(8R^4/3)[A_4(0,2R)-A_4(1,2R)+A_3(1,2R)],$$

$$I_a(sb)=(R^3/3^{\frac{1}{2}})[A_2(1,R)+\tfrac{1}{3}A_0(1,R)],$$

$$I_a(pp)=(8R^4/15)[2A_1(1,2R)+5A_3(1,2R)+5A_4(0,2R)-5A_4(1,2R)+2A_6(0,2R)-2A_6(1,2R)],$$

$$I_a(pb)=(4R^3/3)A_1(1,R),$$

$$I_b(pb)=\tfrac{1}{2}I_a(pb),$$

$$I_a(ps)=(8R^4/3(3)^{\frac{1}{2}})[A_2(1,2R)+A_5(0,2R)-A_5(1,2R)],$$

$$J(ss;bb)=2/R+j(ss;bb)-I_b(bb)-I_a(ss),$$

$$K(sb;sb)=2S/R+k(sb;sb)-S^{\frac{1}{2}}I_b(sb)-S^{\frac{1}{2}}I_a(sb),$$

$$J''(ss;sb)=2S^{\frac{1}{2}}/R+j''(ss;sb)-I_b(sb)-S^{\frac{1}{2}}I_a(ss),$$

$$K(pb;pb)=2S(p)/R+k(pb;pb)-S^{\frac{1}{2}}(p)[I_b(pb)+I_a(pb)],$$

$$J''(ps;pb)=j''(ps;pb)-S^{\frac{1}{2}}(p)I_a(ps),$$

$$J''(pp;sb)=2S^{\frac{1}{2}}/R+j''(pp;sb)-I_b(sb)-S^{\frac{1}{2}}I_a(pp),$$

$$J''(ss;pb)=2S^{\frac{1}{2}}(p)/R+j''(ss;pb)-I_b(pb)-S^{\frac{1}{2}}(p)I_a(ss),$$

$$J''(sp;sb)=j''(sp;sb)-S^{\frac{1}{2}}I_a(ps),$$

$$J''(sb;sp)=j''(sp;sb),$$

$$J''(pb;ss)=2S^{\frac{1}{2}}(p)/R+j''(ss;pb)-S^{\frac{1}{2}}(p)-I_a(pb),$$

$$K(pb;sb)=2S^{\frac{1}{2}}S^{\frac{1}{2}}(p)/R+k(pb;sb)-S^{\frac{1}{2}}(p)I_b(sb)-S^{\frac{1}{2}}I_a(pb),$$

$$K(sb;pb)=2S^{\frac{1}{2}}S^{\frac{1}{2}}(p)/R+k(pb;sb)-S^{\frac{1}{2}}I_b(pb)-S^{\frac{1}{2}}(p)I_a(sb),$$

$$J''(sb;ss)=2S^{\frac{1}{2}}/R+[j''(ss;sb)-I_b(sb)]+I_b(sb)-S^{\frac{1}{2}}-I_a(sb),$$

$$j(ss;bb)-I_a(ss)=(R^5/60)[A_0(1,2R)-5A_4(1,2R)]-(R^4/6)[A_1(1,2R)+A_3(1,2R)],$$

$$k(sb;sb)^{(0)}=(R^7/12)[v_0(3,3,2R)-\tfrac{2}{3}v_0(3,1,2R)+(1/9)v_0(1,1,2R)],$$

$$k(sb;sb)^{(1)}=(R^7/4)[(1/9)v_1(2,2,2R)-(2/15)v_1(2,0,2R)+(1/25)v_1(0,0,2R)],$$

$$k(sb;sb)^{(2)}=(4R^7/135)v_2(2,2,2R),$$

$$\begin{aligned}j''(ss;sb)-I_b(sb)=-[R^3/24(3)^{\frac{1}{2}}]\{&(R^3/2)[B_0(R)A_5(1,2R)+3B_1(R)A_4(1,2R)+2B_2(R)A_3(1,2R)\\&-2B_3(R)A_2(1,2R)-3B_4(R)A_1(1,2R)-B_5(R)A_0(1,2R)]+3R^2[B_0(R)A_4(1,2R)\\&+2B_1(R)A_3(1,2R)-2B_3(R)A_1(1,2R)-B_4(R)A_0(1,2R)]+9R[B_0(R)A_3(1,2R)\\&+B_1(R)A_2(1,2R)-B_2(R)A_1(1,2R)-B_3(R)A_0(1,2R)]+12[B_0(R)A_2(1,2R)-B_2(R)A_0(1,2R)]\},\end{aligned}$$

$$k(pb;pb)^{(0)}=(R^7/4)[v_0(2,2,2R)-\tfrac{2}{3}v_0(2,0,2R)+(1/9)v_0(0,0,2R)],$$

$$k(pb;pb)^{(1)}=(3R^7/4)[(1/9)v_1(3,3,2R)-(2/15)v_1(3,1,2R)+(1/25)v_1(1,1,2R)],$$

$$k(pb;pb)^{(2)}=(4R^7/45)v_2(0,0,2R),$$

$$\begin{aligned}j''(ps;pb)^{(0)}=[R_8/16(3)^{\frac{1}{2}}][&B_1(R)v_0(4,2,2R)+(B_0(R)+B_2(R))v_0(3,2,2R)\\&+(B_1(R)-B_3(R))v_0(2,2,2R)-(B_2(R)+B_4(R))v_0(1,2,2R)-B_3(R)v_0(0,2,2R)\\&-\tfrac{1}{3}B_1(R)v_0(4,0,2R)-\tfrac{1}{3}(B_0(R)+B_2(R))v_0(3,0,2R)-\tfrac{1}{3}(B_1(R)-B_3(R))v_0(2,0,2R)\\&+\tfrac{1}{3}(B_2(R)+B_4(R))v_0(1,0,2R)+\tfrac{1}{3}B_3(R)v_0(0,0,2R)]\end{aligned}$$

$$\begin{aligned}j''(ps;pb)^{(1)}=[3R^8/16(3)^{\frac{1}{2}}][&\tfrac{1}{3}B_2(R)v_1(4,3,2R)+\tfrac{1}{3}(B_1(R)+B_3(R))v_1(3,3,2R)\\&+\tfrac{1}{3}(B_2(R)-B_4(R))v_1(2,3,2R)-\tfrac{1}{3}(B_3(R)+B_5(R))v_1(1,3,2R)-\tfrac{1}{3}B_4(R)v_1(0,3,2R)\\&-\tfrac{1}{5}B_2(R)v_1(4,1,2R)-\tfrac{1}{5}(B_1(R)+B_3(R))v_1(3,1,2R)-\tfrac{1}{5}(B_2(R)-B_4(R))v_1(2,1,2R)\\&+\tfrac{1}{5}(B_3(R)+B_5(R))v_1(1,1,2R)+\tfrac{1}{5}B_4(R)v_1(0,1,2R)],\end{aligned}$$

$$\begin{aligned}j''(ps;pb)^{(2)}=-[R^8/12(3)^{\frac{1}{2}}][&C_1(R)v_2(4,0,2R)+(C_0(R)+C_2(R))v_2(3,0,2R)\\&+(C_1(R)-C_3(R))v_2(2,0,2R)-(C_2(R)+C_4(R))v_2(1,0,2R)-C_3(R)v_2(0,0,2R)],\end{aligned}$$

$$\begin{aligned}j''(pp;sb)^{(0)}=[R^8/16(3)^{\frac{1}{2}}][&(B_0(R)-B_4(R))v_0(2,3,2R)+2B_1(R)v_0(3,3,2R)-2B_3(R)v_0(1,3,2R)\\&+B_2(R)v_0(4,3,2R)-B_2(R)v_0(0,3,2R)-\tfrac{1}{3}(B_0(R)-B_4(R))v_0(2,1,2R)-\tfrac{2}{3}B_1(R)v_0(3,1,2R)\\&+\tfrac{2}{3}B_3(R)v_0(1,1,2R)-\tfrac{1}{3}B_2(R)v_0(4,1,2R)+\tfrac{1}{3}B_2(R)v_0(0,1,2R)],\end{aligned}$$

$$\begin{aligned}j''(pp;sb)^{(1)}=[3R^8/16(3)^{\frac{1}{2}}][&\tfrac{1}{3}(B_1(R)-B_5(R))v_1(2,2,2R)+\tfrac{2}{3}B_2(R)v_1(3,2,2R)-\tfrac{2}{3}B_4(R)v_1(1,2,2R)\\&+\tfrac{1}{3}B_3(R)v_1(4,2,2R)-\tfrac{1}{3}B_3(R)v_1(0,2,2R)-\tfrac{1}{5}(B_1(R)-B_5(R))v_1(2,0,2R)-\tfrac{2}{5}B_2(R)v_1(3,0,2R)\\&+\tfrac{2}{5}B_4(R)v_1(1,0,2R)-\tfrac{1}{5}B_3(R)v_1(4,0,2R)+\tfrac{1}{5}B_3(R)v_1(0,0,2R)],\end{aligned}$$

$$\begin{aligned}j''(pp;sb)^{(2)}=-[R^8/12(3)^{\frac{1}{2}}][&(C_0(R)-C_4(R))v_2(2,1,2R)+2C_1(R)v_2(3,1,2R)-2C_3(R)v_2(1,1,2R)\\&+C_2(R)(v_2(4,1,2R)-v_2(0,1,2R))],\end{aligned}$$

$$\begin{aligned}j''(ss;pb)-I_b(pb)=-(R^3/6)\{&(R^8/8)[(B_0(R)+2B_2(R))A_4(1,2R)+B_1(R)(2A_3(1,2R)+A_5(1,2R))\\&-B_4(R)(A_2(1,2R)+A_0(1,2R))-(2B_3(R)+B_5(R))A_1(1,2R)]+(3R^2/4)[B_1(R)A_4(1,2R)\\&+(B_0(R)+B_2(R))A_3(1,2R)+(B_1(R)-B_3(R))A_2(1,2R)-(B_2(R)+B_4(R))A_1(1,2R)\\&-B_3(R)A_0(1,2R)]+(9R/4)[B_0(R)A_2(1,2R)-B_2(R)A_0(1,2R)+B_1(R)A_3(1,2R)\\&-B_3(R)A_1(1,2R)]+3B_0(R)A_1(1,2R)+3B_1(R)(A_2(1,2R)-A_0(1,2R))-B_2(R)A_1(1,2R)\},\end{aligned}$$

$$\begin{aligned}j''(sp;sb)^{(0)}=(R^8/48)\{&B_1(R)v_0(4,3,2R)+[B_0(R)+B_2(R)]v_0(3,3,2R)+[B_1(R)-B_3(R)]v_0(2,3,2R)\\&-[B_2(R)+B_4(R)]v_0(1,3,2R)-B_3(R)v_0(0,3,2R)-\tfrac{1}{3}[B_1(R)v_0(4,1,2R)\\&+(B_0(R)+B_2(R))v_0(3,1,2R)+(B_1(R)-B_3(R))v_0(2,1,2R)-(B_2(R)+B_4(R))v_0(1,1,2R)\\&-B_3(R)v_0(0,1,2R)]\},\end{aligned}$$

$$\begin{aligned}j''(sp;sb)^{(1)}=(R^8/16)\{&B_2(R)v_1(4,2,2R)+(B_1(R)+B_3(R))v_1(3,2,2R)+(B_2(R)-B_4(R))v_1(2,2,2R)\\&-(B_3(R)+B_5(R))v_1(1,2,2R)-B_4(R)v_1(0,2,2R)-\tfrac{1}{5}[B_2(R)v_1(4,0,2R)\\&+(B_1(R)+B_3(R))v_1(3,0,2R)+(B_2(R)-B_4(R))v_1(2,0,2R)-(B_3(R)+B_5(R))v_1(1,0,2R)\\&-B_4(R)v_1(0,0,2R)]\},\end{aligned}$$

$$\begin{aligned}j''(sp;sb)^{(2)}=-(R^8/36)[&C_1(R)v_2(4,1,2R)+(C_0(R)+C_2(R))v_2(3,1,2R)\\&+(C_1(R)-C_3(R))v_2(2,1,2R)-(C_2(R)+C_4(R))v_2(1,1,2R)-C_3(R)v_2(0,1,2R)],\end{aligned}$$

$$k(pb;sb)^{(0)}=[R^7/4(3)^{\frac{1}{2}}][v_0(2,3,2R)-\tfrac{1}{3}v_0(2,1,2R)-\tfrac{1}{3}v_0(0,3,2R)+(1/9)v_0(0,1,2R)],$$

$$k(pb;sb)^{(1)}=[3R^7/4(3)^{\frac{1}{2}}][(1/9)v_1(3,2,2R)-(1/15)v_1(3,0,2R)-(1/15)v_1(1,2,2R)+(1/25)v_1(1,0,2R)],$$

$$k(pb;sb)^{(2)}=[R^7/45(3)^{\frac{1}{2}}]v_2(0,1,2R).$$

II. Π states

$$I_a(pp)=(R^4/8)\{[B_0(R)-B_2(R)][A_3(1,R)-A_1(1,R)]+[B_1(R)-B_3(R)][A_2(1,R)-A_0(1,R)]\},$$

$$j(p^*p;bb)-I_a(pp)=-(R^4/6)[A_3(1,2R)-A_1(1,2R)]-(R^5/60)[5A_4(1,2R)-6A_2(1,2R)+A_0(1,2R)],$$

$$K(pb;p^*b)=-(R^7/60)[2.5w_1(2,2,2R)-w_1(2,0,2R)+(1/10)w_1(0,0,2R)],$$

$$J''(ps;p^*b)=-[R^8/320(3)^{\frac{1}{2}}]\{[B_0(R)-B_2(R)][5w_1(3,2,2R)-w_1(3,0,2R)]+[B_1(R)-B_3(R)][5w_1(2,2,2R)-w_1(2,0,2R)]-[B_2(R)-B_4(R)][5w_1(1,2,2R)-w_1(1,0,2R)]-[B_3(R)-B_5(R)][5w_1(0,1,2R)-w_1(0,0,2R)]\},$$

$$j''(p^*p;sb)^{(0)}=[R^8/32(3)^{\frac{1}{2}}]\{[B_0(R)-B_2(R)][v_0(4,3,2R)-\tfrac{1}{3}v_0(4,1,2R)]-[B_0(R)-B_4(R)][v_0(2,3,2R)-\tfrac{1}{3}v_0(2,1,2R)]+[B_2(R)-B_4(R)][v_0(0,3,2R)-\tfrac{1}{3}v_0(0,1,2R)]\},$$

$$j''(p^*p;sb)^{(1)}=[3R^8/32(3)^{\frac{1}{2}}]\{[B_1(R)-B_3(R)][\tfrac{1}{3}v_1(4,2,2R)-\tfrac{1}{5}v_1(4,0,2R)]-[B_1(R)-B_5(R)][\tfrac{1}{3}v_1(2,2,2R)-\tfrac{1}{5}v_1(2,0,2R)]+[B_3(R)-B_5(R)][\tfrac{1}{3}v_1(0,2,2R)-\tfrac{1}{5}v_1(0,0,2R)]\},$$

$$j''(p^*p;sb)^{(2)}=-[R^8/24(3)^{\frac{1}{2}}]\{[C_0(R)-C_2(R)]v_2(4,1,2R)-[C_0(R)-C_4(R)]v_2(2,1,2R)+[C_2(R)-C_4(R)]v_2(0,1,2R)\}.$$

Variable Scale Atomic Wave Functions

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In the study of complex atomic spectra by the methods of Slater and Condon, it is desirable that one have a complete set of orthogonal wave functions more nearly correct than the hydrogenic ones. A set of variable-scale wave functions is described in this paper and applied to some simple cases. They are hydrogenic functions of a function of the radius, such that close to the nucleus they behave like the wave functions about a charge Ze and far from the nucleus they behave like the wave function about a charge e. The scale function is chosen so that the integrals arising in calculation can be handled analytically. These functions are not so accurate as the analytic representations of the Hartree functions, but they form a complete orthogonal set, and thus can be used for perturbation problems.

IN The study of complex spectra by the methods of Slater and Condon one needs electronic wave functions which are as nearly correct as possible. The success of the method requires that those nondiagonal terms of the energy matrix corresponding to a change of total quantum number be negligibly small, which in turn requires that the radial parts of the wave function approximate fairly closely to the correct form.

Hydrogenic wave functions are often used, because they form a complete orthogonal set of functions which are possible to handle analytically. However, the correct wave functions differ considerably from the hydrogenic ones, since the effective field on the electron is not a simple coulomb field. A good set of functions to use is the set of analytic representations of the Hartree functions; these can be handled analytically, but they do not form a complete orthogonal set.

The subject of this paper is the investigation of a set of functions which do not correspond to the correct functions as closely as the Hartree ones, but which form a complete orthogonal set which can be handled analytically, and which are much more nearly correct than the hydrogenic type of functions.

The reasoning used in obtaining these functions is somewhat as follows. The effective field on an atomic electron is, to the Hartree approximation, a spherically symmetric coulomb field with an effective nuclear charge which is a function of the distance from the nucleus. The nuclear charge fixes the scale of a hydrogenic wave function. Therefore a hydrogenic wave function whose scale is a function of the distance from the nucleus will be one which corresponds fairly closely to the correct form. A few preliminary tests are made here on this type of wave function to demonstrate its convenience.

THE WAVE FUNCTION

The effective potential V on the electron is spherically symmetric (to the Hartree approximation). The angular factors of the wave function are therefore the usual normalized tesseral harmonics of order m, l, which occur in the hydrogen problem. The behavior of the radial factor S is best expressed by means of the equation for $R \equiv \rho S$ (where ρ is the radial distance in atomic units). This equation is:

$$\frac{d^2R}{d\rho^2}+\left[W-V-\frac{l(l+1)}{\rho^2}\right]R=0,$$

where the energy terms are also in atomic units. The potential V approaches the form $-2Z/\rho$ for small values of ρ and becomes $-2/\rho$ for large values of ρ (Ze is the nuclear charge). If $V=-2Z/\rho$ for all values of ρ, then the characteristic solutions of this equation would be the radial hydrogenic functions, multiplied by ρ:

$$Z^{\frac{1}{2}}N_\rho(2Z\rho/n)^{l+1}e^{-Z\rho/n}L_{n+l}{}^{2l+1}(2Z\rho/n),$$

where $L_{n+l}{}^{2l+1}(x)$ is the $(2l+1)$th derivative with respect to the argument x of the Laguerre poly-

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nomial of order $n+l$, and N_ρ is a normalizing factor $\{(n-l-1)!/n^2[(n+l)!]^3\}^{\frac{1}{2}}$.

However V is not equal to $-2Z/\rho$ for all values of ρ, and we allow for this by letting the scale factor Z change with ρ. Let x be a function of ρ which has the form $x=Z\rho$ when ρ is small and $x=\rho$ when ρ is large. Let $F(x)$ be the function:

$$(2x/n)^{l+1}e^{-x/n}L_{n+l}^{2l+1}(2x/n).$$

Then the function $S(x)=(N_\rho/\rho)(dx/d\rho)^{\frac{1}{2}}F(x)$ is normalized. Also, if x is now a function of ρ containing parameters which are the same for all values of n, $S(n_i)$ will be orthogonal to $S(n_j)$:

$$\int_0^\infty S(n_i)S(n_j)\rho^2 d\rho=\int_0^\infty F(n_i)F(n_j)dx=0,\ n_i\neq n_j.$$

If we can now show that S as defined above is a good approximate solution of the radial equation, the problem of determining the wave function of an atom in any stationary state becomes simply one of determining the parameters in the function $x(\rho)$. For later convenience in calculation it turns out to be advisable to write ρ as an explicit function of x, $\rho=\rho(x)$, rather than to write $x(\rho)$. Now $F(x)$ satisfies the differential equation:

$$\frac{d^2F}{d\rho^2}+\frac{\rho''}{\rho'}\frac{dF}{d\rho}+\left[-\frac{1}{n^2\rho'^2}+\frac{2}{x\rho'^2}-\frac{l(l+1)}{x^2\rho'^2}\right]F=0.$$

Since $R=N_\rho F\rho'^{-\frac{1}{2}}$, R satisfies the equation:

$$\frac{d^2R}{d\rho^2}+\left[\frac{\rho'''}{\rho'^2}+\frac{\rho''}{\rho'}\right]\frac{dR}{d\rho}+\left[\tfrac{1}{2}\frac{\rho'''}{\rho'^3}-\tfrac{1}{4}\frac{\rho''^2}{\rho'^4}\right]R+\left[-\frac{1}{n^2\rho'^2}+\frac{2}{x\rho'^2}-\frac{l(l+1)}{x\rho'^2}\right]R=0.$$

Comparing with the exact equation for R, and taking $-1/(n^2\rho'^2)$ to correspond to W, $-2/(x\rho'^2)$ to V and $l(l+1)/(x\rho'^2)$ to the angular momentum term $l(l+1)/\rho^2$, we see that the approximate equation (of which $\rho'^{-\frac{1}{2}}F(x)$ is an exact solution) contains extra terms: $[(\rho'''/\rho'^2)+(\rho''/\rho')]dR/d\rho$ and $[(1/2)(\rho'''/\rho'^3)-(1/4)(\rho''^2/\rho'^4)]R$. Their presence is not necessarily serious, since the correspondence of the above-mentioned terms to energy, potential, and angular momentum is only approximate, and their presence may actually compensate for this discrepancy, if the parameters in the function are chosen properly.

Thus we have obtained a complete orthogonal set of functions which can be handled analytically if ρ is a simple enough function of x. Presumably a form of ρ can be found which makes R exactly correct, but this form would be so complicated that the functions could not be used. We must sacrifice some accuracy to gain expediency.

According to our discussion of the variation of effective nuclear charge with ρ, we see that ρ must be equal to x/Z for small values of ρ and be equal to x for large values. A function which possesses these properties, and which also makes the various integrals needed amenable to calculation is the following:

$$\rho=x\left[1+\frac{(1/Z)-1}{1+x/c}\right].$$

For this function the various integrals can be expressed in terms of exponentials and integral-logarithms of exponentials.

There remains the parameter c to be fixed so that the set of functions correspond as well as possible to the correct set. This c, once determined, must be the same for all the functions in the set in order that these functions be mutually orthogonal. Its value can be fixed for the problem at hand by various methods, of which two are illustrated in the succeeding section.

Some Applications

One method of fixing the parameter c is by a variational method, giving c the value for which the normal energy is a minimum. For instance, for helium, the energy operator in atomic units is:

$$H=-\nabla_1^2-\nabla_2^2-\frac{4}{\rho_1}-\frac{4}{\rho_2}+\frac{2}{\rho_{12}}.$$

The wave function to be used is $\Psi=Y_1Y_2S(x_1)\times S(x_2)$, where the S's are those discussed earlier (in this case for the normal state) the Y's are constant angular factors, and the x's are related to the ρ's by the equation given above. We then fix c so that

$$I\equiv\int\bar{\Psi}H\Psi d\tau_1 d\tau_2$$

is a minimum. We find for I the expression $I=I_T+I_V+I_{12}$, where

$$I_T=-2\int_0^\infty S\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)d\rho=-8\int_0^\infty\frac{x^2e^{-2x}}{\rho'^2}\left[1-\frac{2}{x}-\frac{7}{4}\left(\frac{\rho''}{\rho'}\right)^2+\frac{\rho'''}{2\rho'}\right]dx,$$

$$I_V=-8\int_0^\infty S^2\rho d\rho=-8\int_0^\infty\frac{F^2(x)}{\rho}dx,$$

$$I_{12}=2\int\frac{Y_1^2Y_2^2S_1^2S_2^2}{\rho_{12}}d\tau_1d\tau_2=64\int_0^\infty x_1^2e^{-2x_1}\int_{x_1}^\infty\frac{x_2^2e^{-2x_2}}{\rho_2}dx_2.$$

Using the relation between ρ and x, we find:

$$I_V=-8[1+c+c^2Ei(-c)],$$

$$I_{12}=\tfrac{1}{4}(5+2c)+4c^2e^cEi(-c)-2c^2e^{2c}Ei(-2c)(c^2-2c+2)+\tfrac{1}{2}c^2(5-2c).$$

I_T is too cumbersome an expression to set down here; its values are given in Table I.

In carrying out the integration of I_{12}, it was found useful to derive a general formula for

$$I_n(\alpha,c)\equiv\int_c^\infty y^ne^{-\alpha y}Ei(-y)dy.$$

Since this may be useful, we give it here:

$$\alpha^{n+1}I_n(\alpha,c)=Ei(-c)n!e^{-\alpha c}\sum_{j=0}^{n}\frac{(c\alpha)^j}{j!}-n!Ei\{-(\alpha+1)c\}+n!e^{-(\alpha+1)c}\sum_{j=1}^{n}\frac{1}{j}\left(\frac{\alpha}{\alpha+1}\right)^j\sum_{\nu=0}^{j-1}\frac{c^\nu(\alpha+1)^\nu}{\nu!}\quad(n\neq0)$$

$$\alpha I_0(\alpha,c)=E_i(-c)e^{-\alpha c}-Ei\{-(\alpha+1)c\}.$$

A plot of I against c shows that $c=4$ is very close to the minimum; we thus take $c=4$, and obtain -5.69 atomic units as the energy of the normal state of helium (to be compared with the experimental value -5.81 atomic units). The Hartree method gives -5.75[1] *Rh.* However, we are not expecting to obtain as good answers as Hartree obtains, but are expecting to get ones better than hydrogenic functions give. This is true, for the hydrogenic functions give -5.5 atomic units for the energy.

TABLE I.

c	$-(I_v+I_{12})$	I_T	$I\equiv I_T+I_v+I_{12}$
1	9.642	4.245	−5.39
2	10.667	5.076	−5.59
3	11.241	5.578	−5.663
4	11.614	5.922	−5.692
5	11.879	6.204	−5.675

[1] Gaunt, Proc. Camb. Phil. Soc. **24**, 328 (1928).

We now give a few checks of our function. It is a consequence of the virial theorem of quantum mechanics, that, for a discrete state of a system with a coulomb potential, the mean potential energy is equal to twice the mean kinetic energy with reversed sign. In our case this means that the exact wave function would give for the ratio $-\frac{1}{2}(I_v+I_{12})/I_T$ the value unity. For $c=4$, we actually obtain the value 0.98 for this ratio (1.008 for $c=3$ and 0.957 for $c=5$).

The diamagnetic susceptibility[2] of helium, since it is a monatomic gas, is given by a universal constant times $\Sigma_i(\rho_i^2)_{00}$. In order to facilitate comparison with experiment we express the measured susceptibility as $\Sigma_i(\rho_i^2)_{00}$ in atomic units. The latter, according to the measurements of Hector and Wills,[3] has the value 2.34.

[2] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, p. 206, Eq. (2), (Oxford, 1932).

[3] Hector and Wills, Phys. Rev. **24**, 418 (1924).

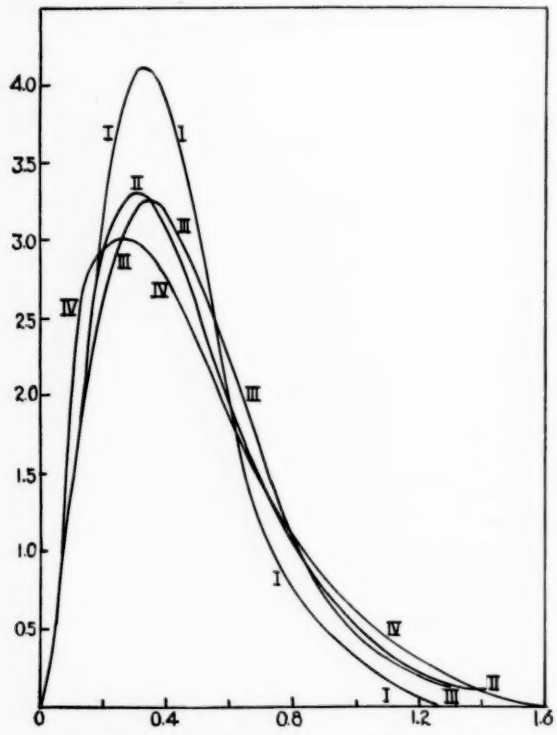

FIG. 1. Electron distribution in normal helium: electrons per Angstrom *vs.* radius in Angstroms. I. Compton-Barrett (from Compton's analysis of Barrett's data on x-ray scattering, II. Hartree, Slater, Hylleraas, III. Pauling, IV. Present method.

Calculation with our wave function gives

$$\sum_i (\rho_i^2)_{00} = (6-3c+5c^2/2-3c^3+7c^4+2c^5) + c^5e^{2c}Ei(-2c)(16+4c),$$

which for $c=4$, has the value 2.82. The error is thus about 20 percent. It should be noted that, unlike ours, most wave functions for normal helium give too low a value for the susceptibility.

We now compare the electron distribution given by our wave function with that given by the functions of Pauling,[4] Slater[5] Hartree,[6] and Hylleraas,[7] and with that calculated by A. H. Compton,[8] by a Fourier analysis of Barrett's data on the scattering of x-rays by helium. Fig. 1 shows our curve ($U=8\pi\rho^2S^2$) and the other curves. Our curve, like the other curves calculated from wave functions, gives a maximum of about three electrons per Angstrom. The disagreement with the curve calculated from scattering data, which gives a maximum of about four electrons per Angstrom, is not to be looked on as serious, since the latter calculation involves a questionable extrapolation in the Fourier analysis.

However, the chief purpose of these wave functions is the calculation of multiplet separations and line intensities by the method of Slater. A rather severe test of their capabilities would be to compute the positions of the $(1s)(2s)^1S$ and $(1s)(2s)^3S$ levels of helium. This test is severe, because the effective electronic field in helium is probably the farthest from spherical symmetry of any atom, and also because for such a small nuclear charge the advantage of the variable-scale functions are not so apparent. For considerably larger values of Z the effective field departs considerably from a coulomb field, and we should expect a variable-scale function to be considerably better than a hydrogenic one.

It turns out that these functions give for $(1s)(2s)$ a singlet-triplet separation of $0.158Rh$ and the center of gravity of the two terms as $-4.201Rh$. The experimental values are $0.058\ Rh$ and $-4.321Rh$, while the values computed from hydrogenic functions are $0.161Rh$ and $-4.08Rh$. The check is not particularly good, but is better than that for the hydrogenic functions. Perhaps a different method of choosing c would give a better check.

Another method of choosing c is to fit the value of the intensity of radiation of a given line to the experimental value. This was done for the case of the D line in sodium ($3^2P\rightarrow 3^2S$). The value of A, the absolute spontaneous transition probability for this transition has been obtained by Minkowski[9] with a fair degree of accuracy; it is 0.64×10^8 sec.$^{-1}$. To obtain this value with wave functions of the type discussed here for $Z=11$, we must have $c=37$.

It is hoped that further calculations with these functions will demonstrate their utility more fully.

[4] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).
[5] J. C. Slater, Phys. Rev. **32**, 349 (1928).
[6] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).
[7] H. Bethe, Zeits. f. Physik **55**, 431 (1929).
[8] A. H. Compton, Phys. Rev. **35**, 925 (1930).
[9] Minkowski, Zeits. f. Physik **36**, 839 (1926).

The Frequency Variation of the Dielectric Constant of Dilute Non-Aqueous Solutions*

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For systems containing polar molecules it has been found that there is a wave-length region in which the dielectric constant decreases with increasing frequency. This wave-length region, dependent upon the size of the orienting molecule and the viscosity of the medium, determines a time of relaxation for the polar molecules which has been evaluated by Debye using the law of Stokes for the rotation of a particle in a viscous medium. The purpose of the present research is to test the dipole theory by making measurements of the frequency variation of the dielectric constant for viscous solutions of various polar substances in nonpolar solvent media. To this end it was necessary to devise an accurate method of measurement for the dielectric constant of a liquid system at frequencies as high as 2×10^8 cycles per second. The apparatus used is briefly described. The dielectric constants of rosin solutions in mineral oils of varying viscosity are tabulated and calculations for the inner-frictional constant for these systems are made. The effect of viscosity upon the behavior of mixtures of "floricin," paraffin oil and vaseline is also investigated. It is found to have little effect, a fact of considerable interest with regard to the inner structure of these solutions. An explanation for the failure to observe an expected dispersion in several experiments is attempted. The comparison of the experimental results with the requirements of the Debye theory leads to several interesting conclusions. There are objections to the use of the ordinary coefficient of viscosity of the medium to measure the frictional resistance to the rotation of a molecule when the discontinuities of the fluid are large compared with the size of the rotating particle and probably in other cases as well. Calculations from the experimental data make possible a differentiation between systems in which the suspended particles are all of one size or monodisperse, and in which they are polydisperse. Finally, there is suggested the type of experiment which must be made if a quantitative verification of the theory is sought.

INTRODUCTION

DRUDE[2] was the first to observe an anomalous dispersion in liquids with short radio waves when he found that many polar substances, such as propyl alcohol, glycerol, etc., showed a decrease in dielectric constant with increasing frequency. Since that time other investigators have made similar observations. However, an explanation of this dispersion was not given until 1913, when Debye[3] attributed it to a transition from the combined effect of deformation and orientation of polar molecules to the effect of the deformation alone. When both deformation and orientation contributions are operative, that is, when the dipoles are swinging with the applied field, the maximum or static dielectric constant is obtained. As the frequency of the applied field is increased the inner-frictional forces between the molecules become effective, and there is produced a phase retardation between the orientation and the applied field. The less complete orientation of the dipoles results in a lower value for the dielectric constant, and an absorption of energy due to this phase difference. When the frequency is increased still further the time between periods becomes so small that no orientation can occur, thus we have only the deformation or distortion effect due to the applied field, resulting in the low, or "optical" dielectric constant. Debye further pointed out that the dispersion caused by this transition will fall in a frequency region determined by the size of the orienting molecule and the frictional constant of the medium. The equation obtained for the dispersion region is

$$0.1<\chi<10, \tag{1}$$

where

$$\chi=[\pi\zeta\nu(\epsilon_0+2)]/[kT(\epsilon_\infty+2)]. \tag{2}$$

In this equation, ϵ_0 is the dielectric constant at

* This article comprises a portion of a thesis presented by J. L. Oncley to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1932.

[1] Charles A. Coffin Fellow in Chemistry, 1931–32.

[2] Drude, Zeits. f. physik. Chemie **23**, 267 (1897) and other references.

[3] Debye, Ber. deut. physik. Ges. **15**, 777 (1913).

zero frequency, ϵ_∞ is the dielectric constant at infinite frequency, k is the Boltzmann constant $=1.37\times10^{-16}$, T is the absolute temperature, ν is the electric frequency in cycles per second, ζ is the "inner-frictional constant," which, when Stokes' law can be applied, is equal to $8\pi\eta r^3$, η is the viscosity of the solution, and r is the particle radius. According to this theory a simple polar molecule, or a monodisperse colloid, should give curves of the forms (a), (b) and (c) of Fig. 1; curve (a) being obtained when we plot the real (observed) dielectric constant (ϵ') against the logarithm of the frequency (log ν), curve (b) when we plot the imaginary dielectric constant (ϵ''), obtained from absorption measurements, against log ν, and curve (c) when we plot the power factor (sin $\tan^{-1}\epsilon''/\epsilon'$) against log ν. If the system is polydisperse, we should find that these curves become flattened out, and that they may be regarded as the result obtained when the simple curves for several particle sizes are added together. Curves of this type are shown by (d), (e) and (f), also of Fig. 1.

The verification of this theory is as yet quite incomplete. Measurements recorded in the literature are sometimes of insufficient accuracy for the purpose because of the unusual experimental difficulties which present themselves, while in other cases the systems studied have hardly conformed to assumptions underlying the theoretical treatment of the problem. Space does not permit review of or even reference to these researches which have been carried out with pure liquids of known chemical composition, articles of commerce such as transformer oils and rubber, and dilute solutions of polar substances in nonpolar solvent media.

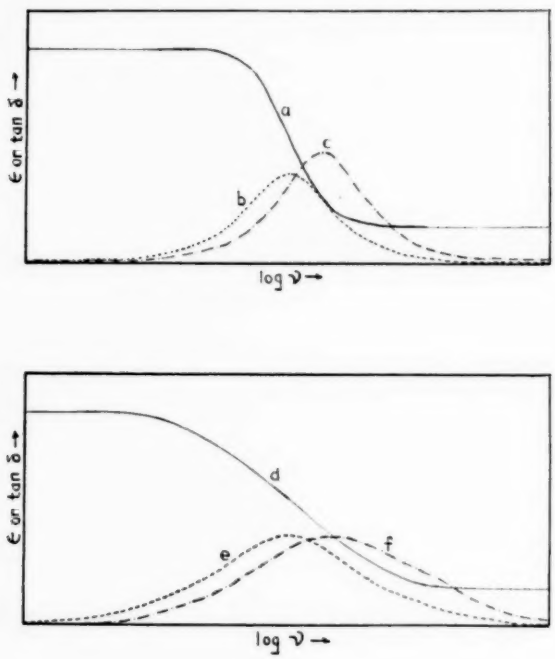

FIG. 1.

The present research was undertaken with the object of finding out what information could be obtained by making accurate measurements of the dielectric constants of viscous solutions of various polar substances in nonpolar solvents. It was decided that the limiting wave-length at which sufficient accuracy could be obtained was about 15 meters. According to the equations of Debye, the frequency ν_c at which the center of the dispersion occurs can be decreased by increasing the inner-frictional constant ζ. If Stokes' law can be applied, this inner-frictional constant is proportional to the viscosity η and to the third power of the radius, r. Accordingly, we should expect a sufficiently high viscosity or a sufficiently large radius to decrease the frequency ν_c until it would fall below 2×10^7 cycles per sec. ($\lambda=15$ meters). When ν_c is found, the value of the inner-frictional constant ζ should be amenable to calculation thus giving a true measure of the friction between solute and solvent molecules or what we may term the "microscopic" viscosity. This microscopic viscosity may then be compared with macroscopic viscosities measured according to well-known procedures.

THEORY

The theory of Debye has been given in detail before,[4] so it will be omitted. Here it is sufficient to say that it leads to the following two equations:

$$\epsilon_{12}' = \epsilon_{12}(\infty) + (\epsilon_{12}(0) - \epsilon_{12}(\infty))/(1+\chi^2), \quad (3)$$

$$\epsilon_{12}'' = \chi[\epsilon_{12}(0)\cdot\epsilon_{12}(\infty)]/(1+\chi^2). \quad (4)$$

In these equations, the subscripts 1 and 2 refer to solvent and solute, respectively, and the subscript

[4] Debye, *Polar Molecules*, Chem. Cat. Co., New York, 1929. It is also reviewed, together with its application to dilute solutions, by Williams and Oncley, Physics 3, 314 (1932).

12 to the binary mixture,

$$\chi = 2\pi\nu\tau_2[\epsilon_{12}(0)+2]/[\epsilon_{12}(\infty)+2],$$

$\tau_2 = (\zeta/2kT)$ is the "time of relaxation" of the polar molecules, which is the time required for $1/e$ of the polar molecules to assume a random distribution after an applied static field has been removed, $\epsilon_{12}(0)$ is the dielectric constant of solution at very low frequencies, $\epsilon_{12}(\infty)$ is the dielectric constant of solution at very high frequencies, $\epsilon_{12}' = \epsilon_{12}'(\nu)$ is the observed ("real") dielectric constant of solution at a frequency ν, $(=[C/C_0] \times[1/(1+4\pi^2\nu^2R^2C^2)])$, $\epsilon_{12}'' = \epsilon_{12}''(\nu)$ is the imaginary dielectric constant of the solution at a frequency ν, $(=[C/C_0][2\pi\nu RC/(1+4\pi^2\nu^2R^2C^2)])$, ζ is the "inner-frictional constant" which, when and if Stokes' law can be applied, is equal to $8\pi\eta r^3$, η is the ordinary macroscopic coefficient of viscosity of the solution, r is the radius of the polar molecules or particles, k is the Boltzmann constant, T is the absolute temperature, ν is the electrical frequency in vibrations per second, C is the pure capacity of cell filled with solution, R is the pure series resistance of cell filled with solution, and C_0 is the capacity of cell in vacuum.

Since each solution has different values of $\epsilon_{12}(0)$ and $\epsilon_{12}(\infty)$, it was found that the calculations could be much simplified by the use of two new functions Δ and Γ, instead of ϵ' and ϵ'', where

$$\Delta = (\epsilon_0-\epsilon')/(\epsilon_0-\epsilon_\infty) = \chi^2/(1+\chi^2) \qquad (5)$$

and

$$\Gamma = \epsilon''/(\epsilon_0-\epsilon_\infty) = \chi/(1+\chi^2). \qquad (6)$$

Further, we have

$$\log\chi = \log\{[\pi(\epsilon_0+2)]/[kT(\epsilon_\infty+2)]\} + \log\zeta + \log\nu. \qquad (7)$$

Now if we plot Δ or Γ against $\log\chi$ we should always arrive at the same form of curve, with changes in ϵ_0, ϵ_∞, and ζ (or τ) causing only a shift of the whole curve along the $\log\chi$ axis. The Δ and Γ curves will have the same general shape as curves *a* and *b* of Fig. 1.

Any monodisperse system (that is, any system with a single value for ζ or for τ) which follows the Mosotti hypothesis should give a curve of this type. Deviations from such a curve can be attributed either to aggregation of the molecules to form polydisperse systems, thus causing several different relaxation times, or to failure for the electrical conditions assumed in the derivation of the Mosotti hypothesis to be satisfied. Thus an extrapolation of deviations from this curve against concentration should give zero as its result. This method has the decided advantage of not employing the molecular weight of either solute or solvent in the calculation—a fact which is of particular use since the molecular weight of the solvent, usually some mineral oil mixture, may be unknown. The calculation of ϵ_2 from ϵ_{12} must involve this molecular weight if it is to be accurate, since the polarization is a partial molar quantity.

It can be seen from Eqs. (3) and (4) that the imaginary dielectric constant will be a maximum, and that the real dielectric constant will take on a mean value at the point where $\chi = 1$. When this is true,

$$[\pi\zeta\nu_c(\epsilon_0+2)]/[kT(\epsilon_\infty+2)] = 1, \qquad (2a)$$

and the critical frequency ν_c is thus given by

$$\nu_c = \frac{\epsilon_\infty+2}{\epsilon_0+2}\frac{kT}{\zeta\pi} = \frac{\epsilon_\infty+2}{\epsilon_0+2}\frac{1}{2\pi\tau}$$

or

$$\nu_c\tau = (\epsilon_\infty+2)/[2\pi(\epsilon_0+2)].$$

After finding this point ν_c where $\chi = 1$, we can calculate ζ from Eq. (2a), since ϵ_0, ϵ_∞, and ν_c are all known. Thus one of the possible applications of these data, which will be discussed further at a later point, is to find this inner-frictional constant, or "microscopic viscosity," ζ.

The Debye theory is not the only theory which accounts for an anomalous dispersion of the dielectric constant and an absorption of energy. However, for the most part, the other theories have been proposed to account for the behavior of complex dielectrics at much lower frequencies. It is well to mention that each of these theories leads to equations of the form

$$\epsilon' = \epsilon_\infty[1+k/(1+4\pi^2\nu^2\tau'^2)] \qquad (8)$$

and

$$\epsilon'' = 2\pi k\nu\tau'\epsilon_\infty/(1+4\pi^2\nu^2\tau'^2), \qquad (9)$$

where ϵ_∞, k, and τ' are given as functions of various measurable quantities, and differ in the

various theories.[5] Gemant[6] has shown that one obtains these equations by simply assuming that the replacement of the equilibrium, when an electrical field is impressed, is an exponential function of the time, thus we have the equation

$$D=\epsilon_\infty(1+k)E-\epsilon_\infty k e^{-(t-t')/\tau'}E, \qquad (10)$$

relating the electric displacement D at the time t to the electric intensity E. Here $\epsilon_\infty(1+k)=\epsilon_0$, τ' is the "time-constant" (or time of relaxation) upon whose value depends the time for equilibrium to be established, and t' is the time at which the field E is applied. This signifies that the displacement at the moment the field is impressed ($t=t'$) is given by $D=\epsilon_\infty E$, and at an infinitely long time ($t=\infty$) by $D=\epsilon_\infty(1+k)E=\epsilon_0 E$.

Thus, any of the important theories of dielectric absorption lead to the same form of frequency dependence of the complex dielectric constant. Accordingly, it can be seen that the only way in which any of these theories can be proved is by the accurate determination of the constants τ', k and ϵ_∞ involved in Eqs. (8) and (9), and subsequent comparison of their values with those calculated by the various theories. Obviously this can only be done for very simple mixtures of pure substances of known composition.

It should be mentioned here that for the most part the Debye theory accounts for losses at very high frequencies (10^8–10^{12} cycles per second), while the others account for losses at much lower frequencies (1–10^6 cycles per second). However, scanty experiments over these ranges indicate that no sharp transition from one region to the other occurs, and that very probably only one absorption region is to be found. Support for the Debye theory may be obtained in that, following arguments based upon the same type of dipole structure, many other effects can be explained. Thus, the data obtained by studies of the Kerr effect, the Stark effect, the infrared rotation bands, and the electric moments of molecules all indirectly support this theory of dielectric absorption of Debye.[7]

Apparatus

The dielectric constants were obtained by determining the capacity of a calibrated cell by means of a modified heterodyne method. The circuit used is given in Fig. 2, and consists of a quartz controlled oscillator and an oscillating detector with one stage of amplification. The quartz crystal vibrated with a fundamental frequency of 1918.9 kilocycles per second ($\lambda=156.2$ meters), and harmonics up to the tenth were present with sufficient intensity to be easily received and used for measurements. The use of the quartz crystal was necessary to insure the stability of frequency in the oscillating circuit. The resonance circuit contained four condensers; an ordinary variable air condenser with which the frequency was adjusted to approximately the proper value, an accurately calibrated standard condenser with a capacity of from 10 to 27 $\mu\mu$f and reading to 0.0066 $\mu\mu$f, a comparison condenser C_4 whose fixed capacity is approximately that of C_x, and a cell C_x into which the solutions were pipetted for the dielectric constant measurements, shown in Fig. 3.

Measurements were made by determining the capacity difference x between C_x and C_4. If the cell is previously calibrated with air and benzene as standards for comparison we can calculate the dielectric constant ϵ of the solution from this difference x in the following manner:

$$\begin{aligned}
&C(\text{air})=C'+C''=C_4+a,\\
&C(\text{benzene})=2.280\times C'+C''=C_4+b,\\
&C'=(b-a)/1.280,\\
&C''=C_4-(b-2.280a)/1.280,\\
&C(\text{unknown})=\epsilon C'+C''=C_4+x,\\
&\epsilon=(C_4-C''+x)/C'=(b-2.280a)/(b-a)\\
&\qquad +1.280x/(b-a)=\alpha+\beta x, \qquad (11)
\end{aligned}$$

where C'' and C' are the fixed and variable portions of cell capacity, respectively, and here equal to approximately 4.9 and 6.1$\mu\mu$f, C(air), C(ben-

[5] Debye's equations (Eqs. (3) and (4)) also reduce to this form, in which case

$$\tau'=\tau(\epsilon_0+2)/(\epsilon_\infty+2) \qquad k=(\epsilon_0-\epsilon_\infty)/\epsilon_\infty \qquad \epsilon_\infty=\epsilon_\infty.$$

[6] Gemant, *Elektrophysik der Isolierstoffe*, J. Springer, Berlin (1930).

[7] For a discussion of such studies, see Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford Press (1932).

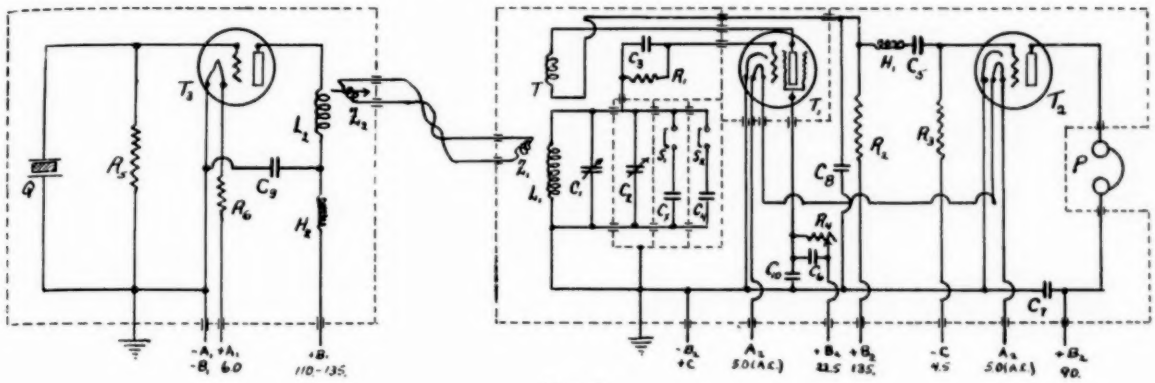

FIG. 2.

C_1 —150$\mu\mu$f variable condenser
C_2 —standard variable condenser
C_3 —250$\mu\mu$f fixed condenser
C_4 —comparison condenser
C_5 —250$\mu\mu$f fixed condenser
C_6 —0.5μf fixed condenser
C_7 —0.5μf fixed condenser
C_8 —200$\mu\mu$f fixed condenser
C_9 —0.001μf fixed condenser
C_{10}—0.5μf fixed condenser
C_x —cell
H_1—radiofrequency choke coil
H_2—radiofrequency choke coil
L_1 —interchangeable inductance coil
L_2 —honey-comb coil tuned to crystal frequency
P —head-phones, 2000 ohms resistance
Q —quartz crystal
R_1 —5×10^6 ohm resistance
R_2 —2.5×10^5 ohm resistance
R_3 —2×10^6 ohm resistance
R_4 —1×10^5 ohm variable resistance
R_5 —2×10^5 ohm resistance
R_6 —5 ohm resistance
S_1 —mercury switch
S_2 —mercury switch
T —tickler coil
T_1 —UV234 vacuum tube
T_2 —UV227 vacuum tube
T_3 —UV171A vacuum tube
Z_1 —pick-up coil
Z_2 —pick-up coil

Batteries as follows:
A_1 —6 volts (storage cells)
A_2 —5 volts a.c. (from transformer)
B_1 —135 volts, or 110 d.c. line
B_2 —135 volts, tapped at 22.5 and 90 volts
C —4.5 volts

zene), and C(unknown) are the capacities of the cell when filled with air ($\epsilon=1$), benzene ($\epsilon=2.280$), and unknown ($\epsilon=\epsilon$). C_4 is the capacity of the comparison condenser, here equal to approximately 17.6$\mu\mu$f, a is the difference in vernier condenser reading (in arbitrary units) when C (air) replaces C_4, b is the difference when C(benzene) replaces C_4, x is the difference when C(unknown) replaces C_4, $\alpha=(b-2.280a)/(b-a)$, and $\beta=1.280/(b-a)$. The accuracy of these measurements, about 1 part in 1000, can be judged from the data of Table I. No corrections for absorption were necessary. Some measurements were also made at two other frequencies, 1000 cycles and 611.1 kilocycles ($\lambda=490.6$ meters), in which cases the customary bridge and resonance methods were used.

The refractive indices were measured with a Pulfrich refractometer in nearly all cases, for the yellow helium line (5876A). In some cases the solutions were not sufficiently clear for this instrument to be used, so that an Abbe refractometer had to be substituted.

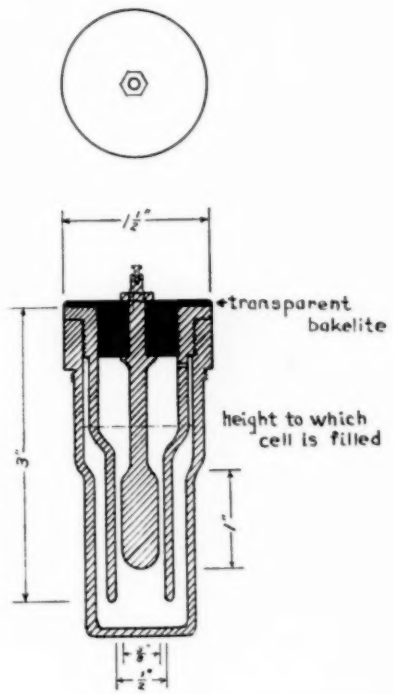

FIG. 3.

The temperature of the cell and of the air used to control the temperature of the crystal oscillator was regulated by means of a thermostat maintained at 25°C. Refractive indices and viscosities were observed at the same temperature. The viscosities were determined by means of a Stormer viscometer, manufactured by the Arthur H. Thomas Company. In this type of instrument the time for 100 revolutions of a cylinder is taken, and from this the viscosity is calculated. The instrument was calibrated by means of sugar solutions of known viscosity.[8] The accuracy of the viscosity determinations was about 5 percent, except in the case of some gels which gave no definite values.

Experimental Data

The experimental results obtained are presented in Tables I–V, inclusive. Table I contains

Table I. *Dielectric constant data for liquids used in this investigation.*

Exp. No.	Substance	ϵ' $\lambda=156.2$ m	$=78.12$ m	$=39.06$ m	$=26.04$ m	$=17.36$ m	mean	n^2
1	Paraffin oil	2.196	2.195	2.196	2.194	2.193	2.194	2.194
2	Finoil	2.154	2.151	2.152	2.154	2.154	2.153	2.146
3	Vaseline	2.079	2.079	2.078	2.078	2.078	2.078	2.190
4	Kerosene	2.138	2.134	2.135	2.135	2.134	2.135	2.100
5	Oleic acid	2.507	2.506	2.507	2.505	2.502	2.502	2.122
6	Carbon tetrachloride	2.244	2.243	2.245	2.241	2.246	2.244	2.130
8	Benzene	2.280	2.280	2.280	2.280	2.280	2.280	2.240

dielectric constant data for the solvents used in this investigation, in addition to those for several other substances. These data have the double purpose of testing the purity of the materials[9] used and the accuracy of the apparatus. The results show that the apparatus is capable of an accuracy of approximately 0.1 percent. The values for benzene are assumed. The values for kerosene seem too high when compared to the square of the refractive index n^2. This is probably caused by the presence of traces of polar substances in the commercial oil. Likewise the values for vaseline seem too low, but this is probably due to an error introduced when the cell is filled with a given volume of melted vaseline and then allowed to cool and contract. Otherwise the agreement is very good.

Table II gives results for various solutions of polar molecules dissolved in mineral oils of high viscosity. With the exception of certain cases in which the No. 5182 cable compound[10] was used as a part of the solvent the dielectric constant is constant over the frequency region studied. The significance of these results will be discussed in the next section.

Table III presents data for solutions of rosin in solvents of various viscosities. The purpose of this particular series of measurements was to study the effect of a viscosity change. The work is somewhat incomplete because of a difficulty in the reproduction of results, probably caused by an oxidation or polymerization of the rosin. The rosin used was of a very high grade, and was finely powdered and added to the hot solvent. When it was practically all dissolved the solution was cooled and filtered through ordinary filter paper under suction. The resulting solution was clear and contained no suspended particles visible to the eye. However, upon standing, a heavy layer of light powder was precipitated and showed that some change was taking place. Further discussion of these results is given later.

Table IV indicates the type of the experiments made upon solutions of "floricin" in oils of various viscosity. Floricin is an oil obtained by distilling castor oil (in this case a U.S.P. grade from Schieffelin and Company) at 300°C until it has lost about 10 percent of its weight. It is a

[8] Data of Bingham and Jackson, Int. Crit. Tab. V, McGraw-Hill Book Company, New York (1926).

[9] Wherever possible the chemicals used were subjected to rigorous purification.

[10] Obtained from the Research Laboratory of the General Electric Company, Schenectady, N. Y.

TABLE II. *Dielectric constant data for systems of polar molecules dissolved in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda = 156.2$ m	$= 78.12$ m	$= 39.06$ m	$= 26.04$ m	$= 17.36$ m	mean	n^2
9	2.6% Nitrobenzene 97.4% Paraffin oil ($\eta = 1.0$)	2.542	2.543	2.543	2.547	2.544	2.544	2.198
10	2.5% Nitronaphthalene 97.5% Paraffin oil ($\eta = 1.05$)	2.435	2.437	2.440	2.440	2.438	2.438	2.204
11	7.4% Oleic acid 92.6% Paraffin oil ($\eta = 0.9$)	2.202	2.202	2.202	2.207	2.205	2.203	2.190
12	26.9% Camphor 73.1% Paraffin oil ($\eta = 3.5$)	3.833	3.839	3.840	3.840	3.847	3.840	2.280
14	7.1% Stearic acid 92.9% Paraffin oil ($\eta > 100$)	2.158	2.157	2.160	2.161	2.156	2.158	2.194
15	4.0% Nitrobenzene 20.0% Vaseline 76.0% Paraffin oil ($\eta > 100$) (Temp. = 6°C)	2.933	—	—	—	2.929	2.931	—
16	3.3% Nitronaphthalene 3.4% Vaseline 93.3% Paraffin oil ($\eta = 6.0$) (Temp. = 6°C supersaturated solution)	2.538	—	—	—	2.538	2.538	—
18	2.8% Nitronaphthalene 64.0% Vaseline 33.2% Kerosene ($\eta > 5$)	2.384	2.386	2.387	2.388	2.387	2.386	—
19	6.0% Nitrobenzene 94.0% Vaseline ($\eta > 100$)	2.769	2.770	2.770	2.768	2.770	2.769	2.194
20	2.5% Nitronaphthalene 97.5% Vaseline ($\eta > 100$)	2.326	2.330	2.328	2.328	2.335	2.329	2.195
21	6.5% Nitrobenzene 25.2% No. 5182 Cable compound 68.3% Paraffin oil ($\eta > 20$)	3.037	3.037	3.036	3.033	3.029	—	2.202
22	Same solution after heating	2.921	2.921	2.920	2.921	2.919	—	2.200
23	6.1% Nitrobenzene 33.7% No. 5182 Cable compound 60.2% Paraffin oil ($\eta > 50$)	3.012	3.012	3.013	3.013	3.012	—	—
24	5.8% Nitrobenzene 94.2% No. 5182 Cable compound ($\eta > 100$)	2.923	2.922	2.922	2.923	2.918	—	—
25	5.4% Nitronaphthalene 94.6% No. 5182 Cable compound ($\eta > 100$)	2.628	2.627	2.627	2.628	2.623	—	—

TABLE III. *Dielectric constant data for solutions of rosin in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda = 3\times10^5$ m	=490.6 m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
26	26.4% Rosin* 73.6% Kerosene	—	—	2.409	2.399	2.393	2.387	2.378	2.173
27	Same one week later	2.427	—	2.422	2.413	2.407	2.402	2.391	2.170
28	20.4% Rosin* 79.6% Finoil	2.309	2.309	2.293	2.288	2.279	2.274	2.271	2.185
29	40.1% Rosin* 59.9% Finoil	—	—	2.403	2.389	2.374	2.364	2.360	2.231
30	26.0% Rosin* 74.0% Paraffin oil	—	—	2.342	2.330	2.323	2.319	2.311	2.233

* Note—The percent rosin refers to the weight of rosin added rather than the weight dissolved.

TABLE IV. *Dielectric constant data for solutions of "floricin" in mineral oils.*

Exp. No.	Composition	ϵ' $\lambda = 3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
31	17.3% Floricin 82.7% Kerosene ($\eta = 0.02$)	—	2.375	2.374	2.375	2.375	2.374	2.115
32	16.5% Floricin 82.5% Finoil ($\eta = 0.4$)	2.391	2.391	2.390	2.390	2.390	2.381	2.151
33	20.8% Floricin 79.2% Finoil ($\eta = 0.5$)	—	2.460	2.458	2.456	2.457	2.450	—
34	15.2% Floricin 84.8% Distilled vaseline ($\eta = 0.4$)	—	2.367	2.365	2.364	2.363	2.359	—
35	15.7% Floricin 84.3% Paraffin oil ($\eta = 1.3$)	2.427	2.429	2.426	2.421	2.417	2.412	2.190
36	20.8% Floricin 79.2% Paraffin oil ($\eta = 1.3$)	—	2.492	2.492	2.491	2.485	2.474	—
37	20.0% Floricin 80.0% Vaseline ($\eta > 50$)	—	2.426	2.422	2.419	2.416	2.410	—
38	18.5% Floricin 28.5% Vaseline	—	2.149	2.149	2.152	2.150	2.148	2.148
39	53.0% Kerosene ($\eta > 0.4$)	—	2.406	2.406	2.408	2.406	2.406	2.148
40	16.5% Floricin 11.5% Kerosene 72.2% Paraffin oil ($\eta = 0.4$)	—	2.417	2.417	2.415	2.412	2.407	—
41	15.1% Floricin 0.8% Vaseline 84.1% Paraffin oil ($\eta > 2$)	—	2.468	2.463	2.463	2.457	2.453	—

TABLE IV. (*Continued*).

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
42	18.6% Floricin 1.9% Vaseline 79.4% Paraffin oil ($\eta>5$)	——	2.461	2.459	2.457	2.449	2.445	——
43	8.4% Floricin 2.5% Vaseline 89.1% Paraffin oil ($\eta>10$)	——	2.309	2.308	2.306	2.302	2.297	——
44	11.0% Floricin 3.9% Vaseline 85.1% Paraffin oil ($\eta>10$)	——	2.350	2.347	2.345	2.343	2.339	——
45	10.7% Floricin 6.4% Vaseline 83.0% Paraffin oil ($\eta>10$)	——	2.339	2.336	2.335	2.333	2.330	2.196
46	15.0% Floricin 30.0% Vaseline	——	2.192	2.188	2.188	2.188	2.182	2.192
47	55.0% Paraffin oil ($\eta>50$)	——	2.390	2.387	2.386	2.384	2.383	2.192
48	10.0% Floricin 15.0% No. 5182 Cable compound 75.0% Paraffin oil ($\eta>10$)	——	2.420	2.418	2.418	2.414	2.410	——

TABLE V. *Dielectric constant data for high molecular weight organic substances in low viscosity solvents.*

Exp. No.	Composition	ϵ' $\lambda=3\times10^5$ m	=156.2 m	=78.12 m	=39.06 m	=26.04 m	=17.36 m	n^2
49	Celluloid in dioxane (sat.)	——	2.476	2.477	2.473	2.470	2.465	2.025
50	10% Masticated pale crepe in CCl_4	2.260	2.253	2.252	2.250	2.255	2.255	2.155
51	Hard rubber in CCl_4 (sat.)	——	2.254	2.255	2.255	2.251	2.250	——

yellowish-brown oil, miscible in all proportions with mineral oils or vaseline,[11] has a refractive index of 1.4771, and a dielectric constant of 4.10 at 156 meters. At lower wave-lengths it shows absorption, in fact this absorption was so strong that no measurements could be made with our apparatus. This oil was chosen because it shows absorption in this region, because it gives readily reproducible results showing little or no dielectric constant change over long periods of time, and because it has a viscosity of the same magnitude as that of the solvent.

There are presented in Table V the results of several miscellaneous experiments. The system celluloid in dioxane shows the beginning of an absorption but the work could not be extended to other solvents because of the insolubility of the celluloid. The pale crepe solutions are either non-polar or else possess an inner-frictional constant too high to permit an orientation. The hard rubber is only very slightly soluble and the results can have little significance since the observed value is so near that for pure CCl_4. Traces

[11] Allen, *Commercial Organic Analysis*, 5th Edition, Vol. 2, p. 228, Blakiston, Philadelphia.

of water might cause errors much larger than the differences observed.

With the exception of experiments 15 and 16, which were made at 6°C, our measurements were carried out at 25°. The dielectric cell had to be recalibrated for the measurements at the lower temperature, by using carbon tetrachloride as the standard liquid.

Viscosities could not always be determined because some of the systems were gels and could give no definite results. The measured viscosity of the gels often changed by a factor of 100 or more. In some cases, however, an estimate of a lower limit could be made.

For the most part the data recorded in the tables are averages of from one to ten sets of measurements for the same solution. In two cases (experiments 38 and 46) there are given the results from a single cell filling which differ considerably from the average of about 10 others (experiments 39 and 47). Their significance will be discussed later.

Discussion

Experiments of this type give important information concerning the application of Stokes' law to the rotary motion of polar molecules in such solutions and suspensions. This has been discussed from a theoretical point of view in a previous paper.[12] In that article the conclusion was drawn that any calculations of molecular size from dielectric constant data for systems of small molecules dissolved in solvents whose molecules are of the same or larger size would be of very doubtful significance. Assuming the correctness of Debye's theory (when ζ is used), it can be seen from the data of Table II that either the law of Stokes cannot be applied or the ordinary coefficient of viscosity fails to measure the frictional resistance to the rotation of the polar molecules. Since no dispersion was observed even at 1.727×10^{7} cycles, the value of the inner-frictional constant ζ must be smaller than 10^{-22} since

$$\zeta=[kT\chi(\epsilon_\infty+2)]/[\pi\nu(\epsilon_0+2)]<(1.37\times10^{-16}\times298\times0.1)/(\pi\times1.727\times10^{7})<1\times10^{-22}.$$

Assuming a molecular radius larger than 2×10^{-8} cm, Stokes' law gives

$$\zeta>8\pi\times(2\times10^{-8})^{3}\eta=2\times10^{-22}\eta.$$

Dispersion should therefore be found in the investigated region when η is larger than $\frac{1}{2}$ poise. All the solutions investigated had viscosities higher than this figure, yet with the possible exception of experiments 21–25 inclusive, no dispersion of the dielectric constant is observed. (Systems containing the No. 5182 cable compound (experiments 21–25) are extremely viscous.)

This conclusion is consistent with the results of experiments of Goldammer[13] and of Weigle and Luthi.[14] These investigators have studied similar systems at wave-lengths as low as 50 cm and have found no dispersion. Certain of these results seem to be in partial disagreement with those of Johnstone and Williams,[15] but a possible and even probable explanation of this difference can now be given.

Table VI. *Calculations from data of Johnstone and Williams.*

% $C_6H_5NO_2$	Viscosity (η)	Inner-frictional constant (ζ)$\times10^{22}$	Radii (assuming $\zeta=8\pi\eta a^3$) in A
16.9	7.7	3.9	1.3
8.7	13.0	10.	1.4
3.1	23.0	9.7	1.2

Calculations from the data of Johnstone and Williams show fairly good agreement with the theory of Debye and are shown in Fig. 4.[16] Table VI gives the observed viscosity values of these solutions, the value of ζ calculated from the curves of Fig. 4, and the molecular radii cor-

[12] Williams and Oncley, J. Rheology **3**, 271 (1931).

[13] Goldammer, Phys. Zeits. **33**, 361 (1932).

[14] Weigle and Luthi, Comptes Rendus **49**, 130 (1932).

[15] Johnstone and Williams, Phys. Rev. **34**, 1483 (1929).

[16] Curve I is obtained from Table II of the original article of Johnstone and Williams, curve II from Table IV, and curve III from Table III.

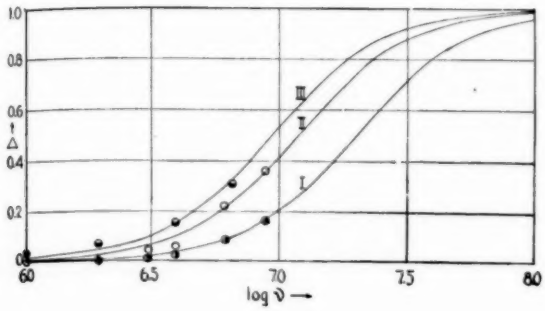

FIG. 4.

responding to these values when Stokes' law in its ordinary form using the macroscopic viscosity of the solution is applied. These radii values are quite small, and should be multiplied by a factor of at least two if agreement with x-ray data is to be obtained. This factor of two then increases ζ by a factor of approximately ten.

Calculations with the data of Mizushima[17] indicate molecular radii of from about 1.7 to 2.5A for the simple alcohols, in good agreement with kinetic theory values. However, at the low temperatures at which the dielectric constant measurements for these substances were made the molecules of these liquids are supposed to be associated. If this is true, one might expect the observed radii to be several times larger than kinetic theory values, which are obtained at much higher temperatures. Accordingly, the application of Stokes' law with the use of the ordinary macroscopic viscosity to measure the frictional rotation of the molecules appears to fail in the determination of ζ by a factor of at least ten. In the case of glycerol this difficulty is much greater, since the calculations give a radius of only 0.35A for this molecule. Another possible explanation of this difficulty in the case of the liquids studied by Mizushima is that it is brought about by the application of the Clausius-Mosotti relationship to polar substances. Experiments of the same type by White and Morgan[18] with certain of the glycols lead to a similar result.

[17] Mizushima, Sci. Papers Inst. Phys. Chem. Research (Tokyo), **5**, 201 (1927); **9**, 209 (1928). Also Debye, *Polar Molecules*, p. 100, Chem. Cat. Co., New York (1929). Recent data of Malsch (Ann. d. Physik [5], **12**, 865 (1932)) are in substantial agreement with these earlier results of Mizushima.

[18] White and Morgan, Physics **2**, 313 (1932). See also the typographical correction in Physics **3**, 53 (1932).

It can be concluded that in the case of all recorded experiments in which the rotation of small molecules has been studied, a failure of Stokes' law by a factor of from ten to several thousand is indicated. This failure may result because such systems do not conform to the law itself or because the use of the macroscopic viscosity in it is not permissible. This discrepancy should be smaller when smaller solvent molecules are used if the application of a law of the form of that of Stokes is justified. Although no definite evidence of this fact is at hand, several of our experiments with floricin and rosin suggest that it is true. We therefore prefer to believe for the present that the discrepancy between theory and experiment has to do with the manner in which in a solution the actual frictional resistance of the solvent molecules to the rotation of the polar solute molecules has been introduced. In other words one might say that the coefficient of viscosity has been introduced into the theory in an inexact way.

The results for the rosin solutions show dispersion, therefore they enable us to see if such systems may be considered theoretically. Since these solutions are probably made up of abiatic acid in various stages of polymerization, we should expect them to behave as polydisperse systems. It can easily be seen that such is the case since the absorption region is spread over a much greater frequency range than for a mono-dispersed system. However, it might be that a single-sized particle would cause absorption in the region investigated. The dielectric constant of any mono-dispersed system can be expressed as a function of the frequency by means of an equation of the form

$$\epsilon(\nu)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)\left[1+\left(\frac{\epsilon_0+2}{\epsilon_\infty+2}\cdot\frac{\zeta\pi}{kT}\right)^2\nu^2\right]^{-1}. \quad (12)$$

Since we have used harmonics of a fundamental frequency ν_0 in this investigation, we may substitute $\nu_i=n_i\nu_0$, and write (12) in the form

$$\epsilon(n_i\nu_0)=\epsilon_i=c+b/(1+an_i^2),$$

where

$$a=[\zeta\pi\nu_0(\epsilon_0+2)]^2/[kT(\epsilon_\infty+2)]^2, \quad b=\epsilon_0-\epsilon_\infty$$

and $c=\epsilon_\infty$. Since this equation involves the three parameters a, b and c, it will be necessary to solve

three equations simultaneously to find their value. Thus taking

$$\epsilon_i = c + b/(1+an_i^2), \qquad \epsilon_j = c + b/(1+an_j^2), \qquad \text{and} \qquad \epsilon_k = c + b/(1+an_k^2),$$

we obtain the following expression for a:

$$a = \frac{\epsilon_i(n_k^2 - n_j^2) - \epsilon_j(n_k^2 - n_i^2) + \epsilon_k(n_j^2 - n_i^2)}{-\epsilon_i n_i^2(n_k^2 - n_j^2) + \epsilon_j n_j^2(n_k^2 - n_i^2) - \epsilon_k n_k^2(n_j^2 - n_i^2)}.$$

Taking the five values obtained for ϵ_i (at the five harmonics where $n_i = 1$, 2, 4, 6 and 9) in all possible combinations of three at a time, we will obtain $5!/(3!\cdot 2!) = 10$ equations, each giving the proper value for a_{ijk} to exactly represent the three dielectric constants ϵ_i, ϵ_j and ϵ_k. If the solution is monodisperse these values should show a random deviation from a mean value due only to experimental errors. On the other hand if the solution is polydisperse there will be a drift of the values toward smaller values of a at the high frequencies, caused by the fact that smaller particles (and hence a smaller ζ and a) are causing the dispersion at the higher frequencies, while the larger particles (larger a) cause the bulk of the dispersion at lower frequencies. The results of such calculations for experiments 26–30 inclusive are shown in Table VII.

The calculations for the systems represented in experiments 26, 27, and 30 clearly indicate polydisperse systems in which the dispersion of the dielectric constant at one end of the region is caused by one kind of molecule and that at the other end by other kinds. However, the calculations from the data of experiment 28, and perhaps from experiment 29 as well, lead to results characteristic of a monodisperse system, since the quantity a is approximately constant and does not show a gradual decrease at higher frequencies. The data used in experiment 28 are average values obtained from five determinations, while experiment 29 is a result obtained from a single series of measurements. The negative value for a_{345} in experiment 29 is probably due to experimental error since small changes in ϵ_3, ϵ_4 or ϵ_5 would give it a positive value. It leads to an

TABLE VII. *Calculations to show size distribution of particles in rosin suspensions.*

Experiment	26	27	28	29	30
a_{123}	0.607	0.500	0.120	0.223	0.640
a_{124}	.291	.284	.087	.165	.436
a_{125}	.163	.340	.089	.166	.242
a_{134}	.079	.094	.085	.089	.180
a_{135}	.048	.040	.090	.111	.079
a_{145}	.028	.050	.098	.169	.035
a_{234}	.023	.036	.083	.058	.079
a_{235}	.016	.014	.090	.083	.032
a_{245}	.012	.005	.101	.170	.008
a_{345}	.009	.0003	.131	(−.514)	.002
mean a	.13	.12	.097	.137	.17
$\zeta \times 10^{21}$	2.4	2.3	2.1	2.5	2.8

imaginary value for ζ; accordingly it has no significance.

The complete interpretation of these results has not been achieved. The experiments were made with solutions which had stood for varying lengths of time, and since polymerization seemed to take place they might be of quite different nature. The rosin suspensions studied in experiments 26, 28 and 29 were made up from 5 to 24 hours before the dielectric constant measurements were made, but those of experiments 27 and 30 were not made until from 8 to 10 days had passed. There is accordingly no relationship between the data of Table VII and the time the suspensions stood before the experimental observations were made. Another possible explana-

tion, but which seems inconsistent with the chemistry of such systems, would be that the Finoil solvent did not allow certain kinds of molecules which were present to dissolve, while they were soluble in kerosene and paraffin oil.

From the average value of ζ we have calculated ϵ_0 and ϵ_∞, and the values for the dielectric constant ϵ' at the various frequencies. These results are presented in Table VIII. As it to be expected the results for experiments 28 and 29 show very

TABLE VIII. *Observed and calculated dielectric constant values for rosin suspensions.*

Experiment	26		27		28		29		30	
Frequency $(\nu)\times10^{-6}$	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
0	——	2.411	——	2.423	——	2.296	——	2.409	——	2.345
1.919	2.409	2.408	2.422	2.421	2.293	2.293	2.403	2.403	2.342	2.341
3.838	2.399	2.401	2.413	2.415	2.288	2.288	2.389	2.389	2.330	2.332
7.676	2.393	2.391	2.407	2.406	2.279	2.279	2.374	2.374	2.323	2.321
11.51	2.387	2.385	2.402	2.400	2.274	2.274	2.364	2.365	2.319	2.316
17.27	2.378	2.382	2.391	2.396	2.271	2.271	2.360	2.360	2.311	2.313
∞	——	2.378	——	2.392	——	2.268	——	2.356	——	2.311

good agreement, while the others are not as good since ζ is not a constant. Although these deviations between the theoretical and observed values are very small because of the small difference between ϵ_0 and ϵ_∞, they show deviations slightly larger than the errors of observation. The results of the calculation of a are much more significant, and they definitely support our conclusions.

The investigations with floricin solutions show an interesting, but at the same time unexpected, behavior. A change in the viscosity η by a factor of several thousand apparently does not change the inner-frictional constant ζ by any large amount. In order to completely establish this as a conclusion it will be necessary to obtain dielectric constant data over a much wider frequency range than our present experiments. It is a fact, however, that the dispersion appears to be about the same in solutions with a viscosity of only a few poises or with a viscosity of several thousand poises. This clearly indicates that the inner-frictional constant ζ changes but little as the viscosity η of the solution is increased.

It appears that these results may be explained by a consideration of the kinetic theory of liquids. Liquids of high viscosity may contain large molecules but they will also contain some smaller ones. Thus a viscous mineral oil consists of long-chain solid hydrocarbons dissolved in shorter-chain liquid hydrocarbons. In a system consisting of polar molecules dissolved in such a solvent we may expect the arrangement of the polar molecules to be such that the frictional forces would be as small as possible. Thus the molecules will tend to arrange themselves in such a way that the inner-frictional constant ζ will be a minimum. If very large molecules are present they may form pockets in which the smaller molecules would have nearly free rotational movement. Thus a small inner-frictional constant ζ will result from any observation designed to measure it. Very small molecules will also have a small inner-frictional constant. Accordingly an increase in the macroscopic viscosity might either increase or decrease the inner-frictional constant. It may also be expected that a variable time of relaxation τ, or inner-frictional constant ζ might result even though the polar molecules were of only one kind, the difference being due to their movements with respect to solvent molecules of various sizes and shapes.

Two experiments with the floricin systems, 38 and 46, show marked differences from the general behavior. Thus, twice in the course of investigation of some fifty solutions results were obtained which gave a constant dielectric constant, its value being equal to the square of the refractive index. In the attempt to duplicate these experiments different values were obtained. In the first case constant but much higher values resulted, but in the second a normal dispersion from higher values was observed. This behavior might possibly be ascribed to experimental error, since a lower value is found if the cell is filled with an insufficient amount of solution or if the solution does not completely fill the space between the two plates of the condenser. However, both times the usual precautions were taken, and it would

be improbable that both times the value obtained would be constant and within experimental error of the n^2 value. It was also noted that the solutions used in those two experiments seemed to be much less heterogeneous than the other solutions of this type. A possible explanation of this difference in dielectric constant values is that because of some difference in heat treatment or perhaps to traces of impurities, a different sort of gel structure which has a much higher inner-frictional constant is formed. In these cases we were completely beyond the dispersion range, while usually we were near its beginning.

These observations are of interest in connection with the results of experiments 21 to 25 inclusive, and with earlier results of Johnstone and Williams. An attempt was made to repeat the earlier work, but unfortunately a sample of the cable compound used to thicken the solvent, "Insulatum B. B.," could no longer be obtained. A thickening substance of the same type, "Cable Compound No. 5182," was used as a substitute, but with only partial success. Certain experiments with systems in which this substance was used show real evidence of a dispersion (21, 24, 25) while others (22, 23) give a constant dielectric constant. The evidence of a positive dispersion effect in the present experiments depends somewhat upon the fact that in the other experiments whose results are given in Table II the observed dielectric constant is slightly higher at 17.36 and 26.04 meters than it is at 156 meters—in other words the experimental error acts in the direction to make the apparent dispersion effect smaller than the effect which should be observed. A comparison of the results of these experiments with those of Johnstone and Williams indicates that in the present systems the effective inner-frictional constant ζ must have a smaller value, probably because of differences in gel structure. The accuracy of the present experiments is considerably greater than that of the earlier work but both show fairly good agreement with the dispersion theory. In a series of recent experiments made at a temperature of -10°C Weigle and Luthi[14] found dispersion taking place at wave-lengths as high as 300 meters in the case of systems of amyl alcohol suspended in a heavy oil (Shell BL3, viscosity 18 poises at 18°C). The results of experiments in which vaseline-like substances are added to a mineral oil in order to prepare a solvent medium of higher viscosity for the solution of polar molecules must always be of lesser theoretical value because the effective inner-frictional constant will vary in a manner which cannot be controlled. This difficulty results from different heat treatments and different structural formations.

In conclusion, it may be said that these results show that the Debye theory, although theoretically sound, is very difficult to apply quantitatively to the existing dielectric constant data. In fact, there seems to be little chance that any data at frequencies below 3×10^7 cycles per second can be quantitatively treated, unless the viscosity of solutions, always made up by using small solvent molecules, is enormously increased by the use of either very low temperatures or very high pressures. The reason for this statement is that any solutions which will show dispersion at such low frequencies must either contain large polar molecules or be prepared from very viscous solvents. At the present time it does not seem readily possible to obtain monodisperse systems either of large molecules or of particles of colloidal size, in nonpolar solvents. Our ordinary solutions and suspensions will exhibit values of ζ which are not constant since particles of various sizes and shapes will be present. Likewise all very viscous nonpolar solvents known to us are made up of several kinds of molecules so that the inner-frictional constant will be poorly defined. Accordingly, further experiments must be made at still higher frequencies to provide an adequate test of the theory. To accomplish this it will be necessary to develop much more accurate methods of dielectric constant measurement than are now at hand, and this task will be a difficult one. A possibility which has much to recommend it is to prepare colloidal solutions of such substances as NaCl, Na_2SO_4, etc., in benzene, carbon tetrachloride, and other pure, nonpolar solvents. These suspensions can be prepared in monodisperse condition by the use of the centrifuge and proper filters. Such experiments were attempted by us, but apparatus for such a purification was not available.

The work is being continued along the lines suggested in the last paragraph.

Dielectric Losses in Rocksalt

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(Received December 9, 1932)

The phase angle of pure dry rocksalt, measured through the range of 1 to 1000 kilocycles, is found to be less than 0.0001. Moisture increases the power factor greatly, especially at the lower frequencies. Traces of surface contamination with certain organic substances may cause rocksalt to have marked apparent dipole properties. The power factor is not measurably affected by prolonged exposure to either intense x-rays or cathode rays.

JOFFÉ[1] states that the conductivity of rocksalt is not markedly increased by x-rays. This fact is consistent with the theory that x-rays displace electrons from the negative chlorine ions, neutralizing the positive sodium ion. It seemed possible that there might be many ions not completely neutralized and yet modified so as to be more loosely bound than in the neutral state. Under alternating fields, the vibration of these ions would be modified, and, thus, the dielectric losses would be changed. Therefore, it was decided to measure the losses at high frequency both before and after coloration with x-rays and cathode rays.

Apparatus

The apparatus was the same as that used by H. H. Race[2] in studying the dielectric properties of an insulating oil. The frequency range used for this study was from 1 to 1000 kilocycles. The standard variable capacitor was a General Radio precision instrument which had been reinsulated with fused quartz. Its power factor, as roughly computed from the dimensions of the plates and of the fused quartz, was of the order of 0.00001.

Preparation and Mounting of Samples

Thin slabs of rocksalt were cut by using a tightly stretched, moistened string about two feet long. A thread tightly wound with fine wire, such as is used in many high resistances, was found to make a very smooth cut. A natural cleavage face of a large block of rocksalt was first ground smooth with fine carborundrum powder and saturated salt solution. To remove traces of the powder, the surface was rubbed over the damp portion of a tightly stretched cloth and then quickly rubbed dry. The polished surface was painted over with paraffin dissolved in toluol. A slice about 2 mm thick was cut off and the polished, paraffined surface melted onto a piece of plate glass. Such a thin layer of rocksalt is easily bent and much care has to be taken in pressing out the paraffin from under it. The second surface was then ground down and polished and the rocksalt sheet removed. The back surface was washed with very pure toluol, gently cleaned with smoothing powder and polished again.

The rocksalt layer was mounted as follows (See Fig. 1): A steel dish *A* was filled with clean

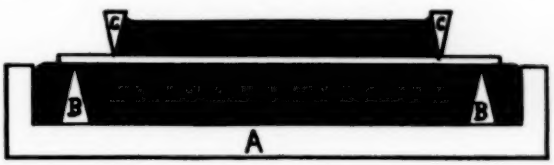

FIG. 1. Condenser mounting.

mercury. An amalgamated brass ring *B*, which was the same height as the dish, was immersed in the mercury. The rocksalt sheet was slid slowly onto the mercury surface so as to entrap no air bubbles. A smaller brass ring *C* was laid upon the rocksalt and was filled with mercury. Contacts were made with the two pools of mercury by amalgamated copper wires.

Procedure and Results

The results of the first test will be described because they show the astonishing effect of certain surface impurities. The surfaces of the

[1] Joffé, *The Physics of Crystals*, McGraw-Hill.
[2] H. H. Race, Phys. Rev. 37, 430–466 (1931).

first sample inadvertently became contaminated with oil. The oil was removed with C.P. benzene and the sample mounted. Tests then showed a remarkably pronounced dipole effect, the power factor being below 0.0005 at 10 and 1000 kilocycles but rising to a sharp peak value of 0.003 at about 190 kilocycles. Later measurements showed that the peak was completely spurious and that it was caused by either slight traces of the oil or the residue from the C.P. benzene. The same sample, after having both surfaces repolished showed no peak at all.

An attempt to use electrodes formed by a carbon paint proved unsatisfactory even though all ingredients were left in a desiccator several days to free them from moisture. The power losses proved to be abnormally high.

A second sample 5 cm×5 cm×1.5 mm was prepared, making a condenser of 67.8 $\mu\mu$f capacity. The surfaces were more highly polished, and the material was more optically clear. The power factor was measured at several frequencies and found to be low and constant. In order to see what effect might be caused by surface moisture, the top electrode was removed and a film of moisture was formed by breathing near it. The electrode was quickly put into place. The power factor was then almost too large to measure and was variable. Measurements were soon stopped when the high-frequency current arced through a crack which had developed in the crystal.

Final measurements were taken on a specially large and pure crystal. The block of rocksalt, 4.5×6×7 cm, was obtained from Ward's Natural Science Establishment. It had been sawed out practically parallel to the natural cleavage planes. It was remarkably transparent and throughout the whole sample had no visible flaw. A plate was cut from the 6×7 face and the polished sheet was 0.9 mm thick. This large surface allowed larger electrodes to be used and produced a condenser of 125.1 $\mu\mu$f capacity. With this increased capacity the accuracy of measurement of the power factor was much improved. The sample was left in a desiccator over night and its power losses measured the next day. It was then colored amber by a 40-minute exposure to x-rays. The sample was about 12 inches from the target of the tube. The potential was 200 kilovolts and the current through the tube was 30 m.a. The sample was again left overnight in the desiccator. The desiccator was placed in a light-tight box so that no fading of the coloration would take place. The upper curve in Fig. 2 shows that the values of the power loss before and after exposure to x-rays are identical. The sample was then given a further exposure to x-rays for two hours. It then had a deep-amber color which, in such a thin layer, represented an intense coloration. It was placed in the desiccator in the dark and, as it happened, was left for four days before

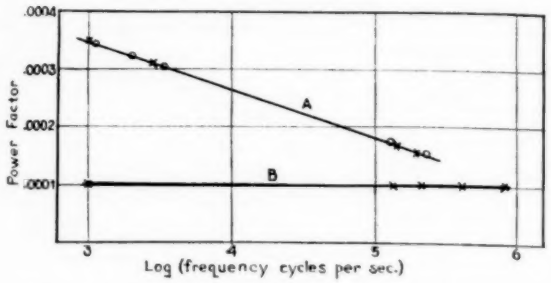

FIG. 2. Curve *A*: the power factor of rocksalt before and after exposure to x-rays; sample dried twelve hours. Curve *B*: the power factor of intensely colored rocksalt after four days of drying.

measurements could be taken. The power factor was then so low that it could not be measured. There was less loss in the sample than in the quartz-insulated standard condenser. Thus the power factor was of the order of 0.0001 or less. If x-radiation had produced any effect, it would have been such as to increase the conductivity and increase the power losses. Therefore, the decided decrease which occurred must have been due entirely to the complete drying which the sample had undergone. To test that point, the sample was left exposed to the humidity of the room (in August) for a day, and then, although it was not noticeably faded, the power factor had increased to nearly the same values as before the coloration.

In order to see if extreme coloration could cause power loss, each surface was exposed 113 seconds to cathode rays from a Coolidge tube. The potential across the tube was 250 kilovolts and the current through the tube was 11 m.a. The sample was about one inch from the metal window of the tube. Both surfaces were colored a blackish brown. This coloration was essentially a surface phenomena. After desiccation for two days the

power factor at 1000 cycles was found to be about 0.1 and was slightly variable. Careful cleaning of the edges of the sample to remove the surface conduction around the edges reduced the power factor to 0.032. The surface coloration was then thoroughly scraped from both sides of the sample for a distance of about five millimeters from all the edges. The sample was then desiccated for two days and one week respectively. The power factor at the end of the week was smaller than at the end of two days and was again less than 0.0001.

Conclusions

Throughout the range of frequency from 10^3 to 10^6 cycles per second and at room temperature: (1) The power factor of pure and thoroughly dried rocksalt is certainly less than 0.0001 and is probably of the order of 0.00001. (2) Slight traces of certain impurities on the surfaces of rocksalt may raise the power factor remarkably at certain frequencies. (3) The effect of moisture on the surface is to increase the power factor considerably, relatively more at low frequencies. (4) Neither intense coloration of rocksalt throughout its body by x-rays nor intense surface coloration by cathode rays appreciably affects the power factor.

The author wishes to thank the General Electric Company for the privilege of conducting this work in its laboratories. Special thanks are due to Dr. H. H. Race of the Research Laboratories for his interest and help in the investigations and to S. I. Reynolds of the General Engineering Laboratories who carefully made all the bridge-settings.

The Magnetic Susceptibilities of Lead, Silver and Their Alloys

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(Received January 12, 1933)

The magnetic susceptibilities of lead, silver and their alloys have been determined by a modified Curie balance. They may be expressed by $10^9\chi=(116.44\pm0.68)+(0.764\pm0.012)P$, P being the weight percent of silver. The anomalous results reported previously by Spencer and John in regard to the magnetic behavior of these alloys are not confirmed.

THE general behavior of the magnetic susceptibilities of alloys of nonferromagnetic metals has been established by numerous investigators,[1] and certain rules may be laid down regarding it. In particular, if the alloy series consists of a heterogeneous mixture of two phases, then the magnetic susceptibility should vary linearly with the composition by weight from the value of one phase to the value of the other. The validity of this rule seems obvious, and in addition it has been well checked by careful observers. Therefore, it is quite surprising to find in the literature, several alloy series which appear flagrantly to disobey it. Spencer and John[2] in 1927 investigated a number of alloys of the noble metals, silver and gold, with a base metal, lead, tin or cadmium. None of these alloys behaved as would be expected. In particular, lead and silver are practically insoluble in each other, and their alloys of all compositions consist of merely mechanical mixtures of lead and silver. The magnetic susceptibility of these alloys should then vary linearly from the value of lead to that of silver. This was not found to be true, and, in fact, alloys containing from 3.6 percent to 47.6 percent by weight of lead were found to be strongly paramagnetic, notwithstanding the fact that both pure lead and silver are diamagnetic. The present work was undertaken to reinvestigate this phenomenon.

The apparatus used for the measurement of the magnetic susceptibilities was a modified Curie balance which has been previously described.[3] For this work an electrodynamometer was added so that the force on the beam in the magnetic field could be balanced out by the force between two current-carrying coils. A device for additional damping was also used which consisted of a small sheet of aluminum attached to the beam. This aluminum was in a magnetic field produced by a small electromagnet. The electromagnetic damping could be easily controlled by changing this field and was adjusted until the motion of the beam was critically damped. Care was taken to avoid the production of convection currents in the room. It was found that these improvements contributed materially to the convenience for use and to the accuracy of the apparatus.

The magnetic susceptibilities were determined by comparison with a standard of gold of purity 99.99 percent or better obtained from Baker and Company. It was cut in the form of a small cylinder of about the same size as the alloy samples. Its susceptibility per gram was taken[4] as -141.0×10^{-9}. The susceptibility per unit volume of air was taken as 29×10^{-9}, and hence the susceptibility of the standard relative to air as -142.5×10^{-9} per gram. The current necessary to balance out the deflection of the sample was determined for several values of the field strength. At each field strength four readings of the current were taken, reversing either the direction of the field or the compensating current

[1] K. Honda and T. Soné, Sci. Rep. Tohoku Univ. [1] **2**, 1–14 (1913); H. Endo, ibid. **14**, 479–512 (1925); recently F. L. Meara, Physics **2**, 33–41 (1932).

[2] J. F. Spencer and M. E. John, Proc. Roy. Soc. **A116**, 61–72 (1927).

[3] Carol G. Montgomery, Phys. Rev. **36**, 498–505 (1930).

[4] H. J. Seeman and E. Vogt, Ann. d. Physik [5] **2**, 976–990 (1929).

each time in order to eliminate any effect of stray fields upon the electrodynamometer. Similar determinations were made for the effect of the holder and the standard at each run of the apparatus. All the measurements were made within a few degrees of 20°C. The masses of the alloys were determined on an analytical balance with calibrated weights. The densities were computed from the relation[5] $v=0.09551-0.0000760p$, where v is the specific volume in cubic centimeters and p the weight percent of lead. The susceptibilities were then computed from the expression: $\chi_a=\chi'(m'/m)[(i_a-i_h)/(i'-i_h)]+\kappa/\rho$, where χ_a is the susceptibility of the alloy per gram relative to vacuum, χ' the susceptibility of the standard relative to air; m and m' the masses of the alloy and the standard respectively; i_a, i_h, i' the currents necessary to compensate for the alloy plus holder, the holder, and the standard plus holder respectively; κ the volume susceptibility of air; and ρ the density of the alloy.

The alloys of high silver content were made from the pure materials by fusing in quartz in an oil-pump vacuum. The rest were fused in a graphite crucible in air, by using a cover of molten borax to prevent oxidation. The melts were allowed to cool quickly to prevent any tendency for segregation. The crucibles were broken away and the alloys cut to a convenient size either on a lathe or with a clean file. Care was taken to prevent contamination before melting. After the sample was prepared, it was necessary to clean the surface carefully to get rid of ferromagnetic impurities. This was accomplished by a prolonged etching in a 5 percent solution of nitric acid in alcohol. The etching process was continued until a constant value of the susceptibility was obtained. The samples were small cylinders about one centimeter long and weighed between two and five grams.

After the magnetic measurements were complete, the samples were rolled out and sampled for analysis by clipping. The analysis was effected by making a corrected fire assay for the silver, the lead being determined by difference. The fire loss amounted to between 2 and 3 milligrams of silver for a 100-milligram button and was determined from two blanks. The percentage of silver present was determined to within an estimated error of one-third of one percent. Although tests were made, both by microscopic examination and by means of analysis, no evidence for segregation was obtained. The authors wish to express their sincere thanks to Mr. W. E. Milligan of the Hammond Metallurgical Laboratory of Yale University for carrying out these cupellations.

[5] E. Maey, Zeits. f. physik. Chemie **38**, 295 (1901).

TABLE I. *Measurement of diamagnetic susceptibilities.*

Alloy	% Ag by weight	Mass (g)	Diamagnetic susceptibility per g$\times 10^9$
Lead *a*	0	4.851	116.0
" *b*	0	5.466	119.5
" *c*	0	5.770	115.1
" *d*	0	5.767	116.1
1	10.6	4.845	122.9
2	10.9	4.558	125.0
3	21.6	4.807	133.1
4	26.4	4.055	135.8
5	27.3	4.152	136.5
6	38.4	3.340	144.1
7	39.6	4.284	146.4
8	47.4	4.663	158.3
9	68.4	2.695	170.2
10	80.8	4.046	178.6
11	85.5	2.220	182.6
Silver *a*	100.0	2.514	190.2
" *b*	100.0	2.141	191.4
" *c*	100.0	3.715	194.4

Table I contains the results of these measurements. Each value of the susceptibility given in the table is derived from the mean of twenty or more readings of the electrodynamometer current, taken at several values of the field strength and in several cases at quite different times. There was never observed any variation of susceptibility with the strength of the field, and hence the samples may be regarded as free from ferromagnetic impurities. The separate values listed for pure lead and silver were obtained from as many different melts. These values are represented graphically in Fig. 1. It is impossible to represent Spencer's and John's reported values on this figure as they extend to a paramagnetic susceptibility of 2000×10^{-9}.

The mean deviation of the susceptibilities from the mean susceptibility for each sample amounts to 2.23×10^{-9} per gram or from 1 to 2 percent. As the analyses of the alloys are more accurate than this, we may find by least-squares methods the best straight line to fit the points, regarding the percentages of silver as accurate.

The result of such a computation is $10^9\chi = (116.44 \pm 0.68) + (0.764 \pm 0.012)P$, where P is the weight percent of silver. The points fit the line closer than is to be expected. The value of 0.6745 $[\Sigma v^2/(n-2)]^{\frac{1}{2}}$, where v is the residual, is 1.15×10^{-9}, while computing the probable error of a single observation by $0.8453 \times 2.23 \times 10^{-9}$ (Peter's method), we get 1.88×10^{-9}. As this value is larger than the other, it was adopted and the probable errors in the expression for the susceptibility computed from it. By this means it is possible to get more accurate values of the susceptibilities of pure lead and silver than by direct observations. The values so determined are, per gram,

$$\text{for lead} \quad \chi = (116.4 \pm 0.7) \times 10^{-9},$$

$$\text{for silver} \quad \chi = (192.8 \pm 0.8) \times 10^{-9}.$$ [6]

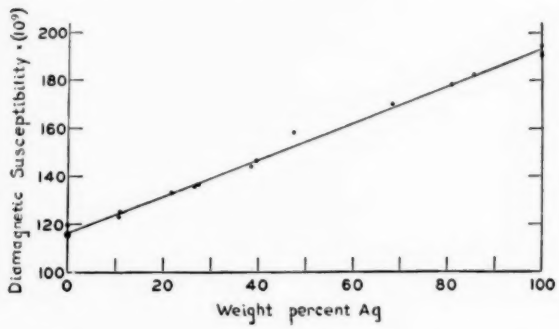

FIG. 1. Diamagnetic susceptibility of lead-silver alloys as a function of silver content.

Thus, it is shown that lead-silver alloys do behave as expected within the observation errors of these experiments.

It remains to suggest that the results of Spencer's and John's work are incorrect because of iron contamination. The values determined above are all more diamagnetic than theirs. Their magnetic field was comparatively weak, of the order of one thousand gauss, and iron contamination has a larger effect at low field strength. Hence it appears probable that this is the reason for the anomalous behavior of the alloys that Spencer and John measured.

In conclusion, the authors wish to express their thanks to Professor L. W. McKeehan for his helpful guidance, and the senior author to the Sterling Fellowship Fund for financial assistance.

[6] These experiments offer no support to so low a value as $\chi_{Ag} = 179.4 \times 10^{-9}$ found by E. Vogt, Ann. d. Physik [5] 14, 1–39 (1932).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The C State of Li_2

Some time ago[1] the writer called attention to the fact that a simple Heitler-London calculation makes the known $^1\Pi S^N$ state[2] of Li_2 repulsive, in qualitative disagreement with experiment. A later calculation showed that the modified method proposed by Slater,[3] which takes account of the influence of the corresponding polar state, gives just the same results as the ordinary Heitler-London treatment.

Thus it appears that the mutual polarization of the two atoms, neglected in the simple Heitler-London calculation, is of decisive importance, and that the inclusion of the polar wave functions does not account for any appreciable part of this influence. The direct description of the polarization given by Rosen[4] for the ground state of H_2 is instructive; but this procedure is not available in other problems, since it does not take account of the effects of inner electrons. The correct modification in the general case has been indicated by Eisenschitz and London.[5] One must use as wave function a linear combination of the original Heitler-London wave function with similar functions for other molecular states. The program of successive approximations given by Eisenschitz and London is not well suited to actual calculation, as is illustrated by their very poor results for the ground state of H_2. Slater[6] has pointed out that the best way to get accurate results in practice is to treat the problem as if it were degenerate and obtain the energy from a secular equation.

A good example of a successful application of this procedure is provided by the work of Ireland[7] on the BeH molecule. In the case of the ground state of BeH the inclusion of the influence of a single higher state sufficed to change complete disagreement with experiment into good qualitative agreement. Thus though the simple Heitler-London method itself fails in this case, a modification which does not unduly increase the labor involved gives good results.

In the present note the writer wishes to call attention to the fact that such a result cannot be obtained in the case of the C state of Li_2. In Table I are listed some of the atomic configurations which can give rise to $^1\Pi S^N$ states of Li_2. It is seen that there are a number of higher states whose influences should be of the same sort and which are about the same distance from the C state, and that there are an infinite number less than twice as far away as the nearest. Thus to give a correct account of the influence of polarization one would have both to calculate the influences of a considerable number of states and to show that the influence of states lying still higher is negligible.

TABLE I.

Configuration	Energy (in Rh)	Distance above $2\,^2S+2\,^2P$
$2\,^2S+2\,^2P$	−0.657	0.000
$2\,^2P+2\,^2P$	−0.521	0.136
$2\,^2S+3\,^2P$	−0.511	0.146
$2\,^2S+3\,^2D$	−0.508	0.149
$2\,^2S+4\,^2P$	−0.461	0.196
$2\,^2S+4\,^2D$	−0.459	0.198
$2\,^2S+4\,^2F$	−0.459	0.198
$\lim_{n\to\infty}[2\,^2S+n\,^2(P, D, F, \cdots)]$	−0.396	0.261

The influence of the $^1\Pi S^N$ state arising from the $2\,^2P+2\,^2P$ configuration is probably somewhat smaller than those of the states next above it, but its influence can be calculated much more readily. The calculation shows that the C state, at the distance at which the experimental curve has its minimum, is pushed down by roughly one-tenth the amount required to make it agree with experiment. This is a reasonable share of the effect for this state to have, if one supposes that a considerable number of higher states also play an appreciable part.

There is no reason to suppose that this is a very exceptional case. We are led to the conclusion that the Heitler-London method, which has great value as a general approach to valence problems, is likely even in very simple cases to fail to give us any feasible way to explain quantitatively the position of a state. The reliability of general rules based on first order Heitler-London studies seems to be in part a mysterious coincidence.

An alternative way of attack is to use two-center functions, as Hylleraas[8] did for H_2. This has been attempted for the C state of Li_2. The motion of the π electron, being nearly hydrogenic, presents no difficulty; but for the σ

[1] W. H. Furry, Phys. Rev. **39**, 1015L (1932).

[2] Named by Mulliken, Rev. Mod. Phys. **4**, 1 (1932), the C state.

[3] J. C. Slater, Phys. Rev. **35**, 509 (1930).

[4] N. Rosen, Phys. Rev. **38**, 2099 (1931).

[5] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).

[6] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[7] C. E. Ireland, Phys. Rev. **43**, 329 (1933).

[8] E. A. Hylleraas, Zeits. f. Physik **71**, 739 (1931).

electron the effect of the K-shells cannot be neglected even in first approximation, and an attempt to use a variation method here leads to integrals whose numerical tabulation is not feasible.

The difficulties in the diatomic fixed-nuclei problem come from the necessity of taking into account both the effect of inner electrons and that of polarization. The use of atomic wave functions, characteristic of the simple Heitler-London method and its modifications, gives a ready account of the effects of inner electrons, at the expense of introducing complications when the effect of polarization is important. The procedure then required is clearly defined by the work of Eisenschitz and London and in this note we have seen an example of what an unpleasant situation will sometimes result. In the two-center method the original assumption disposes of the effect of polarization, and we are left with the problem of dealing with the effects of the inner electrons, which, except in H_2, are always important. This problem would seem to deserve more attention than it has received so far, since its solution might provide a method of treating valence problems which could give satisfactory results where the atomic-function method cannot.

WENDELL H. FURRY

University of California,
December 28, 1932.

Lack of Observed Hyperfine Structure in the Al III Line, 5722.6A

Tolansky[1] has reported attempts to obtain the hyperfine structure of lines of Al III with a Fabry-Perot etalon, using a high potential discharge in a liquid air cooled hollow cathode lamp. Because of broadening of the fringes by reason of Stark effect, negative results were obtained.

Recently we have attempted to obtain the hyperfine structure of the Al III line at 5722.6A, given by the transition $4s^2S_{\frac{1}{2}}-4p^2P_{\frac{1}{2}}$. Use was made of a Fabry-Perot etalon and a Shüler lamp with a spark gap in series. In order to excite the lines with sufficient intensity to photograph them, it was necessary to run the cathode at a temperature near the melting point of aluminum. Etalon separations of 1, 3, 5, 8, and 12 mm were used. Visual observation of the various photographed interference patterns failed to reveal any evidence of structure. Microphotometer records show that the fringes are very symmetrical and are quite broad, having a half-width of 0.10A; in fact the Doppler broadening of the fringes is such that high resolutions cannot be obtained. A careful study of the small irregularities on the records led to the conclusion that they are due entirely to plate grain. The symmetrical shape of the curves indicate either that there is no structure to the line at all, or that the structure consists of two very close unresolved components of approximately equal intensity or several still closer components. The vapor-pressure of aluminum is so low that it is impossible to excite Al III lines without at the same time introducing other effects which make the determination of the hyperfine structure very difficult.

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GEORGE B. SABINE

Department of Physics,
Cornell University,
February 1, 1933.

[1] S. Tolansky, Zeits. f. Physik **74**, 336–43 (1932).

Emission of γ-rays by Nuclei Excited by Neutrons, and Nuclear Energy Levels

Neutrons seem to be remarkably efficient in the excitation of atomic nuclei with which they unite. When nitrogen, by the impact of a neutron is converted into boron and helium, mass is lost (energy equivalent to 1.4 million electron-volts), if Aston's mass values are entirely correct. In the disintegrations with capture of the neutron which have thus far been investigated, kinetic energy has either been conserved, or a part of it has disappeared and presumably has been transformed into γ-rays.

While examining half a dozen photographs of the disintegration of nitrogen obtained by Gans, Newson and the writer, two remarkably good (A) photographs were found which represent capture of the neutron. These are marked (HA) in Table I, where they are compared with results from three of the best photographs obtained by Feather (FA), together with four (FB) from slightly imperfect, and five less perfect (FC) photographs.

If the rest masses alone of N^{14} and n^1 are considered the rest mass of the newly formed N^{15} is 15.0147 ± 0.004, which undoubtedly represents an excited state of this nucleus. In addition there has been 0.002 or more mass units of kinetic energy to dispose of in the cases which have thus far been investigated. The excess energy is presumably emitted as a γ-ray.

TABLE I. *Amount of energy (in 10^6 electron-volts) which disappears in the reaction and is presumably converted into γ-rays.*

	$N^{14}+n^1 \rightarrow N^{15} \rightarrow B^{11}+He^4$				
1.	1.4	(*HA*)	1.4 (*FB*)	1.3 (*FC*)	
2a.	2.3	(*HA*)	2.0 (*FB*)	2.0 (*FB*)	2.3 (*FC*)
	2.8	(*FA*)	2.5 (*FC*)		
3.	3.8	(*FA*)	3.8 (*FA*)	3.9 (*FB*)	
4.	5.0	(*FC*)	5.8 (*FC*)		

A possible explanation of the constancy of the lowest value, 1.4×10^6 electron-volt as found in the table, is that this value is due to this amount of error in Aston's mass values. Obviously the error may be in any or all of the four masses involved.

On the basis of the last paragraph the amount of energy which is converted into γ-rays in the disintegration process would be as shown in Table II which also strongly suggests differences between definite energy levels.

TABLE II.

1.	0.	0.	0.	
2.	0.9	0.6	0.6	0.9
	1.4	1.1		
3.	2.4	2.4	2.5	
4.	3.6	4.4		

Obviously additional accurate data related to the disintegrations are needed to give definite evidence that such levels exist. Also more accurate mass values are needed in order to determine if mass is transformed into radiation and to give the correct values for the table. Table I seems to indicate the type of relation which exists, since it seems improbable that the rest masses on the two sides of the equation should be exactly equal, but this difference may be very small, in which case Table II would give more nearly the energy transformed.

WILLIAM DRAPER HARKINS

University of Chicago,
February 11, 1933.

Schroedinger's Rule and Hydrodynamics

§ 1. The rules given by E. Schroedinger[1] for the derivation of stress-tensors from Lagrangian functions of mechanical and electromagnetic types:

$$S_{\rho\sigma}=\bar{\psi}_\rho\frac{\partial L_m}{\partial\bar{\psi}_\sigma}+\psi_\rho\frac{\partial L_m}{\partial\psi_\sigma}+\phi_\rho\frac{\partial L_m}{\partial\phi_\sigma}-\delta_{\rho\sigma}L_m \qquad (1)$$

$$T_{\rho\sigma}=\frac{\partial L_e}{\partial(\partial\phi_\rho/\partial x_\alpha)}\frac{\partial\phi_\sigma}{\partial x_\alpha}+\frac{\partial L_e}{\partial(\partial\phi_\alpha/\partial x_\rho)}\frac{\partial\phi_\alpha}{\partial x_\sigma} \qquad (2)$$

do not always give symmetric tensors satisfying the laws of conservation. The requirement that these tensors (or their sum, if the Lagrangian function L is of mixed type) should fulfill these requirements may, perhaps, be used tentatively as a criterion for the selection or rejection of Lagrangian functions for variation problems of physical interest. In this connection it is interesting to note that Schroedinger's rule gives the correct stress-tensor

$$S_{xx}=\rho u^2+p, \qquad S_{xy}=\rho uv=S_{yx}$$

when it is applied to

$$L_m=\rho\left[\frac{d\phi}{dt}+\alpha\frac{d\beta}{dt}-\tfrac{1}{2}(u^2+v^2+w^2)\right]-f(\rho),$$

$$\left(\frac{d}{dt}=u\frac{\partial}{\partial x}+v\frac{\partial}{\partial y}+w\frac{\partial}{\partial z}\right)$$

the modified Lagrangian function of Clebsch,[2] which becomes equal in absolute magnitude to the pressure p when the quantities u, v, w, α, β, ρ, and ϕ satisfy the Eulerian equations obtained by giving these quantities independent variations. The equations of equilibrium (laws of conservation) are also satisfied on account of these Eulerian equations, that is

$$\partial S_{xx}/\partial x+\partial S_{xy}/\partial y+\partial S_{xz}/\partial z=0.$$

§ 2. It should be noticed that in his Eq. (27) in which he gives the complete tensor $T_{\rho\sigma}+S_{\rho\sigma}$ derived from a Lagrangian function L, Schroedinger uses the symbol $S_{\rho\sigma}$ for the tensor previously denoted by $S_{\sigma\rho}$. In other words, the expression in our Eq. (1) is denoted later by the symbol $S_{\sigma\rho}$. A reason for this change may be found by considering first a Lagrangian function L which is a function of quantities $g_{mn}=\frac{1}{2}(\phi_m\psi_n+\phi_n\psi_m)$. The rule (1) gives

$$S_{\rho\sigma}=g_{\rho\alpha}(\partial L/\partial g_{\sigma\alpha})+g_{\rho\sigma}(\partial L/\partial g_{\sigma\sigma}).$$

On the other hand, if we consider a Lagrangian function L which is a function of the quantities $g_{mn}=\frac{1}{2}(\partial\phi_m/\partial x_n+\partial\phi_n/\partial x_m)$, the rule (2) gives

$$T_{\rho\sigma}=g_{\sigma\alpha}(\partial L/\partial g_{\rho\alpha})+g_{\sigma\rho}(\partial L/\partial g_{\rho\rho}),$$

thus the change from $S_{\rho\sigma}$ to $S_{\sigma\rho}$ is desirable for consistency.

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Norman Bridge Laboratory,
Pasadena, California,
February 15, 1933.

[1] E. Schroedinger, Ann. d. Physik **82**, 265 (1927).

[2] Clebsch, J. f. Math. **56**, 1 (1859); H. Bateman, Proc. Roy. Soc. London **A125**, 606 (1929).

An X-Ray Examination of the Harmonic Thickness Vibration of Piezoelectric Quartz Plates

The mode of thickness vibration of a piezoelectric quartz plate, whose period is determined by the thickness of plate, is generally known to be very complicated. I. Koga[1] has, however, shown that the thickness vibration of a plate cut parallel to $(10\bar{1}1)$ net plane (the so-called R-cut plate), if the dimension of the surface is sufficiently large as compared with the thickness, is of a pure shear, the displacement being in the direction of an electric axis of the crystal and further that, in such a plate as an oscillator, the vibration of each harmonic can be sustained separately. In the first harmonic there are two planes of loop of the vibration coinciding with both surfaces, while in the third harmonic two more planes of loop become added inside the plate. The reduction of extinction for x-ray reflection would be most remarkable in the loops where the inhomogeneity of deformation is maximum.

An experimental evidence for the above consideration can best be given by the Laue photographic method. An R-cut plate was prepared in the form of rectangular plate, $0.543\times2.94\times3.24$ cm^3, the longest side being parallel to the electric axis. Photographs were taken with rays from a tungsten tube at 60 kilovolts incident normally on the central portion of the plate and collimated by two slits (0.5×4.0 mm^2) the height of which was set parallel to

[1] I. Koga, Physics **3**, 70 (1932).

$(1\bar{2}10)$ plane of the crystal. As is well known,[2, 3] the pattern obtained from the nonoscillating plate showed double lines. Oscillating the sample by an ordinary Pierce circuit in its first harmonic (cycle $=4.5\times10^5$), the component lines of each doublet are enhanced and widened towards each other as is seen in Fig. 1, which leave between them

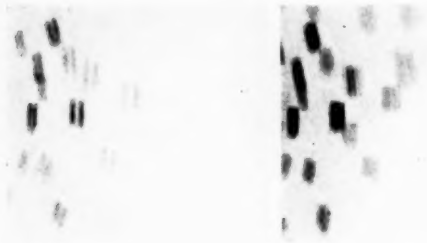

FIG. 1.

FIG. 2.

a weak region which corresponds to the median nodal plane of vibration. Fig. 2 gives the pattern when oscillated in its third harmonic. Here we see that, besides the general increase of the reflection from the interior part of crystal, the doublets are replaced by four lines corresponding to four planes of loop of the third harmonic.

If the shearing motion takes place only in the direction of electric axis, we could expect the increase of the intensity of x-ray reflection very great for such net planes as $(1\bar{2}10)$, but relatively small for ones as $(\bar{1}011)$. To test this point a spectrometric measurement was made by transmitting Mo $K\alpha$ radiation through a similar R-cut plate, $0.258\times3.1\times3.2$ cm^3. The result was as just expected, *viz.*, the reflection from the net plane $(\bar{1}011)$ was found to suffer little effect while that of the $(1\bar{2}10)$ plane to show a large increase of intensity by the vibration. In the latter case, the intensity under oscillation with the plate voltage of 396 volts in the exciting circuit, was about four times, for the fundamental (cycle $=9.5\times10^5$), and about twelve times, for the third harmonic, that observed when the plate was at rest. Further the effect was examined through different parts of the plate, and no remarkable variation was found except in the neighborhood of the boundary of the plate, from which it may be concluded that the plate oscillates in a simple mode, having planes of loop and node as is required from the theory. A full account will be published in the *Scientific Papers of the Institute of Physical and Chemical Research.*

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Y. SAKISAKA
I. SUMOTO

The Institute of Physical and Chemical Research, Tokyo, January 25, 1933.

[2] C. S. Barrett, Phys. Rev. **38,** 832 (1931).

[3] S. Nishikawa, Y. Sakisaka and I. Sumoto, Phys. Rev. **38,** 1078 (1931).

Thermodynamic Calculations from Spectroscopic Data[1]

The most laborious step in the calculation of thermodynamic functions from spectroscopic data is the evaluation of the Q-sum, when the levels are not taken as those of a rigid rotator plus one or more harmonic oscillators. Giauque and Clayton[2] have shown how to calculate the rotational Q-sum for any one vibrational level, when the rotational levels are given by

$$\epsilon_r = B_v m^2 + D_v m^4 + F_v m^6 + \cdots,$$

where $m = j + \frac{1}{2}$. The rotational constants can usually be represented by $B_v = B_0 + \alpha v + \beta v^2$; $D_v = D_0 + \gamma v$; $F_v = F_0 + \delta v$. In any case, by the use of expressions similar to these, Eq. (5b) of Giauque and Clayton may be written as a power series expansion

$$Q_r(v) = K_0 + K_1 v + K_2 v^2 + \cdots,$$

where terms up to v^4 will ordinarily be sufficient. It is the purpose of this communication to show how the complete Q-sum may be obtained without term by term summation.

The energies of the vibrational states are

$$\epsilon_v = h(v\omega_e + v^2\omega_e x + \cdots).$$

The complete Q-sum is

$$Q = \sum_{v=0}^{\infty} Q_r(v) \exp\left[-(h/kT)(v\omega_e + v^2\omega_e x + \cdots)\right].$$

If we expand the anharmonic correction factor $\exp\left[-(h/kT)(v^2\omega_e x + \cdots)\right]$ as a power series in v^2, we get

$$Q = \sum_{v=0}^{\infty} P(v) z^v,$$

where $P(v)$ is a power series in v, and

$$z = e^{-h\omega_e/kT}.$$

This series can be summed, term by term, by using the following formulas.

$$(1-z)\sum_{v=0}^{\infty} z^v = 1,$$

$$(1-z)^2\sum_{v=0}^{\infty} v z^v = z,$$

$$(1-z)^3\sum_{v=0}^{\infty} v^2 z^v = z(1+z),$$

$$(1-z)^4\sum_{v=0}^{\infty} v^3 z^v = z(1+4z+z^2),$$

$$(1-z)^5\sum_{v=0}^{\infty} v^4 z^v = z(1+11z+11z^2+z^3),$$

$$(1-z)^6\sum_{v=0}^{\infty} v^5 z^v = z(1+26z+66z^2+26z^3+z^4).$$

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Giauque and Clayton, J. Am. Chem. Soc. **54,** 1731 (1932).

It is possible to write an explicit formula for the final Q, but this does not seem desirable. By working out the power series, step by step, it is much easier to cut off the expansions at the right point.

The occurrence of several oscillations, with both anharmonic and coupling terms, causes no difficulty. Thus, for the energy

$$\epsilon=\omega_1 u(1-xu)+\omega_2 v(1-zv)-yuv$$

we have, using only the first two terms of the expansion,

$$Q=\sum_{u=0}^{\infty}\sum_{v=0}^{\infty} s^u t^v(1+au^2+buv+cv^2)$$
$$=ST+as(1+s)S^3T+bst S^2T^2+ct(1+t)ST^3,$$

where

$$s=e^{-h\omega_1/kT} \qquad S=1/(1-s),$$
$$t=e^{-h\omega_2/kT} \qquad T=1/(1-t),$$
$$a=hx\omega_1/kT \qquad b=hy/kT \qquad c=hz\omega_2/kT.$$

If the frequency ω_2 is doubly degenerate, a factor $(v+1)$ is introduced before summing. It may happen in such a case that the anharmonic term involves the azimuthal quantum number l. This causes no trouble, since a preliminary summation over l, by using such formulas as

$$\sum_{l=0}^{v} l=v(v+1)/2,$$

$$\sum_{l=0}^{v} l^2=v(v+1)(2v+1)/6,$$

will always give a power series in v.

It is not necessary to give detailed formulas for the various possible cases; the method is sufficiently flexible so that it may be applied to almost any situation which will be met in practice, with a considerable saving in computation. It is clear, of course, that the temperature derivatives of Q may also be obtained in this way.

The accuracy of the results is limited almost entirely by the number of terms used in the expansions; the only unavoidable error is that of replacing the sum over rotational terms by an integral; this error does not affect the leading term in the expansion, and makes but a slight difference in the other terms. The unavoidable error in Q_r will certainly be less than 0.01, which would be less than one part in 10^5 for most applications; to calculate the entropy to 0.001, the accuracy needed in Q is only one part in 2000.

This method has been applied to check various calculations in the literature, with excellent results. It will be used also in a forthcoming work from this laboratory dealing with the entropy and free energy of nitrous oxide.

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Light Excitation in Neon by Lithium Ions

In view of the recent experiments of Beeck[1] and Beeck and Mouzon[2, 3] on the threshold values for ionization of the noble gases by alkali ions, it was thought worth attempting to observe directly the potential at which light excitation occurs. Since Güntherschulze and Keller[4] have found neon to be more strongly excited than other gases in low potential discharges, we have tried Li^+ on Ne for which Beeck and Mouzon determined an ionization potential of 307 volts.

The lithium ions were produced by a heated platinum filament coated with spodumene as described by Bainbridge.[5] The ions were accelerated through a distance of 3 mm by potentials ranging from 150 to 550 volts. The beam was collimated by a hole, 6 mm in diameter and 10 mm long, the end of which was covered by a fine nickel gauze. Upon leaving the collimating slit, the ions entered a field free observation chamber 1.7 cm long at the end of which was a large cylindrical collector connected to a galvanometer to measure the ion current. The parts of the tube exposed to light from the filament were coated with a carbon deposit to prevent scattering.

The gas pressure was so regulated that no discharge appeared when the accelerating potential was applied to the tube with the filament on or off. This procedure prevented a beam of Ne^+ ions entering the observation space. The neon used had no spectroscopic impurities.

The light intensity of the beam of Li^+ ions in Ne was compared photometrically with the light from a 10 watt lamp appropriately screened to reduce the light intensity and to obtain an approximate color match. While no photometric settings could be made below 200 volts, the light from the beam could be detected as low as 160 volts. Before these measurements were taken the observer sensitized his eyes for faint light by remaining in total darkness for 15 minutes.

That the light of the beam was due to excitation of Ne rather than of the Li^+ was determined by replacing the collector cup by a flat plate and applying a retarding field for the ions in the observation space. The length of the luminous beam decreased in a regular manner with the increase of retarding potential. It was found that the luminous beam stopped short of the retarding plate while the field was still low enough to permit the ions to reach the plate.

Secondary electrons produced at the collimating slit by

[1] O. Beeck, Ann. d. Physik **6**, 1001 (1930).

[2] O. Beeck and J. C. Mouzon, Ann. d. Physik **11**, 737 (1931).

[3] O. Beeck and J. C. Mouzon, Ann. d. Physik **11**, 858 (1931).

[4] A. Güntherschulze and F. Keller, Zeits. f. Physik **72**, 143 (1931).

[5] K. T. Bainbridge, J. Frank. Inst. **212**, 317 (1931).

the impact of Li^+ ions had no effect upon the measurements since their measured velocity was too small to produce excitation in Ne. The results were the same no matter whether the potential of the collector was the same as, slightly greater, or slightly less than the plate containing the collimating slit.

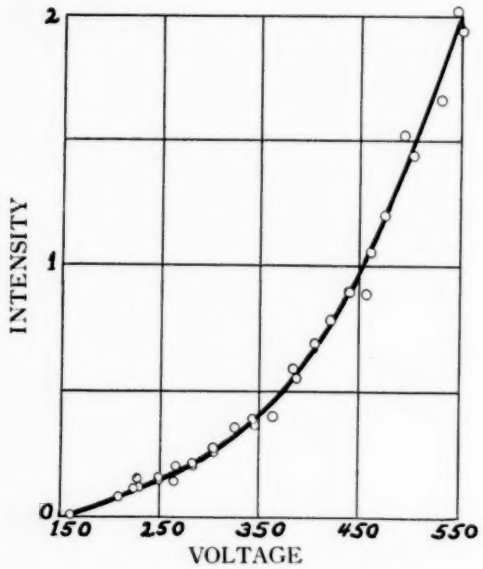

FIG. 1.

The curve shown in Fig. 1 is a composite of four sets of readings. The curves were adjusted by fitting the 386 volt point. The light intensity zero indicates the minimum light intensity observable.

It is interesting to note that light excitation by the Li^+ ions in Ne can be observed approximately 150 volts below the potential at which Beeck and Mouzon observed the beginning of ionization. The curve showing the variation of light intensity with voltage approaches the axis in an asymptotic fashion, whereas Beeck and Mouzon's ionization curve approaches the axis sharply. The fact that Beeck and Mouzon observed a sharp onset of ionization may be due to the fact that the accuracy of their method is limited by the sensitivity of the electrometer for collecting the ion current. In their apparatus the appearance of negative current was observed and taken to indicate the ionization of the gas. However, photoelectrons set free by the radiation excited may have been present at much lower voltages.

These measurements on excitation of light by alkali ions in the noble gases are being extended and a more complete report will be published in the near future.

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January 27, 1933.

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The Plasticity of Rocksalt and Its Dependence upon Water

In a letter with the same title Mr. Bowling Barnes communicates the fact that rocksalt crystals after being soaked in water and then dried on the surface, show infrared absorption which depends on the water soaked into the crystal.[1] The suggestion that the entrance of water into the rocksalt crystals is possible and, moreover, may be connected with the high plasticity of "wet" rocksalt, first was introduced by me[2] and not by Polanyi and Ewald, as Barnes incorrectly states. In collaboration with Quittner, moreover, I have shown that the electric conductivity of rocksalt increases by soaking and subsequent drying of the surface. By this fact an indirect proof of the entrance of water into the crystal was given.[3] The direct spectroscopic finding of water in the crystal by Barnes is a most satisfactory proof and an essential completion of our former results. It will be of great interest to measure the quantity of water per cc by the method of Barnes.

Whether the high plasticity of wet rocksalt can find sufficient explanation by these results, I, nevertheless, regard as uncertain.

The opinion of Joffé that the high tensile strength of wet crystals is induced by healing of the fissures of surface without any assistance of plasticity, we have disproved by experiment,[4] as well as the suggestion of Polanyi and Ewald that watering effects a reduction of the elasticity limit below the tensile strength of dry rocksalt. In fact, dry rocksalt has a limit of elasticity less than the tensile strength,[5] agreeing quantitatively with the limit of elasticity for wet rocksalt.[6]

Experiments on the rupture of dry rocksalt crystals[7] as well as on the dependence of tensile strength on temperature[8] indicate that rupture starts from surface fissures generated by plastic deformation. By levelling the surface of crystals such disturbances may be eliminated, with the result that rupture occurs only at markedly higher tensile stresses. Moreover, it must be remembered that the high tensile strength of wet rocksalt has been proved only for very small cross sections. If the translation planes in the case of small cross sections effect less significant surface

[1] R. B. Barnes, Phys. Rev. **43**, 82 (1933).

[2] A. Smekal, Naturwiss. **16**, 743, 1045 (1928); Phys. Zeits. **32**, 187 (1931).

[3] F. Quittner and A. Smekal, Zeits. f. physik. Chemie **B3**, 162 (1929); Phys. Zeits. **32**, 187 (1931).

[4] A. Smekal, Phys. Zeits. **32**, 187 (1931); U. Heine, Zeits. f. Physik **68**, 591 (1931).

[5] A. Smekal, Phys. Zeits. **31**, 229 (1930); F. Blank, Zeits. f. Physik **61**, 727 (1930).

[6] K. H. Dommerich, Zeits. f. Physik **80**, 242 (1933); G. F. Sperling, Zeits. f. Physik **74**, 476 (1932).

[7] A. Edner, Zeits. f. Physik **73**, 623 (1932). H. Schönfeld, Zeits. f. Physik **75**, 442 (1932).

[8] W. Burgsmüller, Zeits. f. Physik **80**, xxx (1933).

cracks the increase in tensile strength might be connected with the rapid diminution of cross section by soaking in water.

The two last-mentioned explanations remain valid when the crystal surface is levelled with other solvents; on the other hand, it is possible that some solvents do not enter into the crystal. We have found that soaking rocksalt in concentrated sulfuric acid, as well as with H_2SO_4+25 percent SO_3 gives exactly the same results as with water, the same fact was proved for potassium iodide crystals when placed in water or methyl alcohol.[9] It would be of great importance if the spectroscopic method of Barnes could be extended to these cases.

The penetration of water into rocksalt crystals indicates the existence of fissures and crevices, as Barnes has pointed out. We have directly made visible such inhomogeneities of rocksalt by photoelectric[10] and ultramicroscopic methods.[11] Contrary to Barnes, however, we should not suppose a connection with the secondary structure of crystals as postulated by Zwicky. As recently shown by Orowan,[12] the calculations of Zwicky are incorrect. Incorrect[13] also are the statements of Buerger concerning changes of the translation mechanism in the group of alkali halides[14] which Zwicky claims as a proof of a secondary structure in rocksalt and the other alkali halides.[15] There is at present no theoretical or experimental support for the existence of a Zwicky secondary structure in rocksalt. As far as I see, the same situation holds for every other crystal. The beautiful results of Goetz with bismuth crystals are consistent with the existence of inhomogeneities which are not regularly distributed in the interior of crystals.

ADOLF G. SMEKAL

Institut für theoretische Physik der
Universität Halle,
February 1, 1933.

[9] E. Rexer, Zeits. f. Physik **72**, 613 (1931).
[10] A. Smekal, Wien, Akad. Anz. 1926, p. 195; 1927, pp. 22, 46.
[11] E. Rexer, Zeits. f. Physik **76**, 735 (1932).
[12] E. Orowan, Zeits. f. Physik **79**, 573 (1932).
[13] Cf. W. Schütze, Zeits. f. Physik **76**, 135, 149 (1932).
[14] M. J. Buerger, Amer. Min. **15**, 114, 226 (1930).
[15] F. Zwicky, Helv. Phys. Acta **4**, 49 (1931).

The Mass of Be^9 and the Atomic Weight of Beryllium

The mass of Be^9 was measured from five spectra as 9.0155 ± 0.0006 units on the $O^{16}=16$ scale. Be^{9+} was compared with C^+ by means of the ratios $Be^{9+} : C^{12+} :: C^{12+} : CH_4^+$. In Fig. 1, spectrum 1 is a reproduction of a contact print of one of the spectra of this type. The mass of Be^9 was also compared with that of Ne^{20++} by use of the approximate ratios $Be^{9+} : Ne^{20++} :: C^+ : CH^+$ as shown in Fig. 1, spectra 1 and 2. The value obtained from five

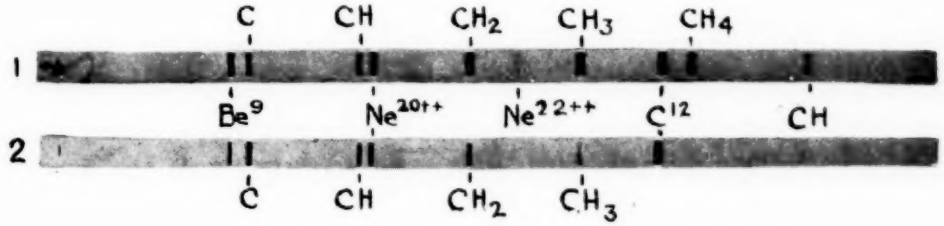

FIG. 1. Mass-spectra of Be^9 and associated lines. Natural size.
(1) $Be^{9+} : C^{12+} :: C^{12+} : CH_4^+$. (2) $Be^{9+} : Ne^{20++} :: C^{12} : CH^+$.

spectra by using this latter ratio was 9.0154 ± 0.0008 when referred to $Ne^{20}=19.9967$.[1] The other reference masses were $C^{12}=12.0036$ and $H^1=1.00778$ as given by Aston.[2] Attempts to measure the mass of Be^9 by the ratios $Be^{9+} : O^{++} :: OH_2^+ : O^+$ have not succeeded so far as oxygen appears to be "cleaned up" in the presence of the $BeCl_2$ used to provide the beryllium ions. Except for the runs in which oxygen was present a satisfactory source of Be ions was provided by the evaporation from the cathode of anhydrous $BeCl_2$ with subsequent ionization in a discharge run in neon. This type of source has been described before.[3]

There are several interesting considerations which follow from this determination of the mass of Be^9.

(1) It appears improbable that the nucleus of Be^9 consists of two α-particles and one neutron,[4] or of two α-particles and one proton and one electron, as the sum of the masses of the suggested components is less than the mass of the stable Be^9 nucleus.

(2) Allowing for the presence of one part in 2000 of Be^8,[5] the atomic weight of beryllium on the chemical scale is 9.0130 ± 0.0007, which is considerably lower than the value

[1] K. T. Bainbridge, Phys. Rev. **43**, issue of March 15, 1933. Paper presented before American Physical Society, Dec. 28, 1932.
[2] F. W. Aston, Proc. Roy. Soc. **A115**, 487 (1927).
[3] K. T. Bainbridge, Phys. Rev. **39**, 847, 1021 (1932).
[4] F. Perrin, C. R. **194**, 1343 (1932).
[5] W. W. Watson and Allan E. Parker, Phys. Rev. **37**, 167 (1931).

9.0179 ± 0.0009 which Hönigschmid and Birkenbach[6] obtained by chemical means.

(3) The packing fraction of Be^9 is $+17.2$ which is located well off the packing fraction "curve" for elements of even atomic number.

(4) Curie and Joliot[7] have calculated the mass of Be^9 and obtained a value 9.0109 on the $O^{16}=16$ scale under the assumptions that $Be^9+\alpha \rightarrow C^{12}+$neutron, that the energy of the neutron is 7.8×10^6 electron-volts, that no γ-rays are emitted in the process of disintegration, and that the Be neutrons have the same mass as the B neutrons. On the other hand the work of Meitner and Philipp[8] and of Rasetti[9] in conjunction with that of Becker and Bothe[10] strongly indicates that γ-rays do accompany the emission of neutrons from beryllium when it is bombarded by α-particles. Taking the process of disintegration to be $Be^9+\alpha \rightarrow C^{12}+$neutron$+h\nu$ and the mass of Be^9 to be 9.0155 and the mass[11] of the neutron 1.0067, 12.1×10^6 electron-volts are available for the energies of the neutron and γ-ray. Under this mode of disintegration 7.8×10^6 electron-volt neutrons[7] might be accompanied by 4.3×10^6 electron-volt γ-quanta. It is an open question whether the γ-rays found experimentally,[12] are produced as a primary process in the disintegration of the beryllium or whether, as indicated in the recent experiments of Auger,[13] the γ-rays are produced by a secondary process as a result of inelastic neutron impacts in nearby materials. The production of γ-rays by both processes may of course take place concurrently.

(5) Sufficient energy is available from the combination $Be^9+\alpha+E_\alpha$ so that a large number of disintegration mechanisms are theoretically possible. The evidence available at present is best satisfied by the reaction $Be+\alpha \rightarrow C^{12}+$neutron$+h\nu$. The experiments which have been performed up to the present time have not been such as to eliminate alternative modes of disintegration. One such possible mechanism, for example, might be $Be^9+\alpha \rightarrow 3\alpha+$neutron$+h\nu$, which might be a "capture" or a "non-capture" process.

Although the measured mass of Be^9 cannot be used at present for an evaluation of the mass of the neutron, it is hoped that this Be^9 mass determination may help ultimately in the solution of the questions attendant on the disintegration of beryllium by different agents.

The author wishes to take this opportunity to thank Dr. A. Bramley for the benefit of his criticisms, discussions, and interest; Dr. W. F. G. Swann for his interest and support, and Professor John A. Miller and Dr. M. Kovalenko of the Swarthmore College Observatory for their generous permission to use their measuring instruments.

K. T. BAINBRIDGE

Bartol Research Foundation of the
Franklin Institute,
February 10, 1933.

[6] O. Hönigschmid and L. Birkenbach, Ber. Chem. Ges. **55B**, 4 (1922). The atomic weight of beryllium from the ratio $BeCl_2/Ag$ is given as 9.0179 with a "mean error" ±0.0013.

[7] I. Curie and F. Joliot, Nature **130**, 57 (1932); I. Curie, F. Joliot and P. Savel, C. R. **194**, 2208 (1932).

[8] L. Meitner and K. Philipp, Naturwiss. **20**, 929 (1932).

[9] F. Rasetti, Zeits. f. Physik **78**, 165 (1932).

[10] H. Becker and W. Bothe, Zeits. f. Physik **76**, 421 (1932).

[11] J. Chadwick, Proc. Roy. Soc. **A136**, 692 (1932). The mass of the neutron is 1.0067 ± 0.0010 from Chadwick's disintegration data and Aston's mass values for N^{14}, B^{11} and He^4 (reference 2). The probable error has been calculated here in the customary manner on the basis that Aston's limits of error are equal to three times the probable errors of his measurements. Two other sets of data permit an upper and a lower limit to be placed on the mass of a neutron, assuming the existence of only one type of neutron.

The emission of neutrons by the process $Li^7+\alpha \rightarrow B^{10}+n$ gives an *upper limit* for the mass of a neutron 1.0063 ± 0.0008 from the mass data of J. Costa (Ann. de Physique **4**, 425 (1925)) and F. W. Aston (reference 2) and the disintegration experiments of I. Curie, F. Joliot and P. Savel (reference 7) and M. de Broglie and L. Leprince-Ringuet (C. R. **194**, 1616 (1932)).

If the nucleus of H^2 is composed of one proton and one neutron, 1.0057 ± 0.0002 is a *lower limit* for the mass of a neutron (K. Bainbridge, Phys. Rev. **41**, 115 (1932)).

[12] Wilson chamber β-ray tracks in a magnetic field, I. Curie and F. Joliot, C. R. **194**, 708, 1229 (1932). P. Auger ibid., 877. By absorption and coincidence method, H. Becker and W. Bothe, Naturwiss. **20**, 757 (1932) and reference 10; F. Rasetti, Naturwiss. **20**, 252 (1932).

[13] P. Auger, C. R. **196**, 170 (1933).

Cosmic-Ray Bursts

In cloud-chamber experiments the frequent occurrence of associated tracks has been observed.[1] It has been pointed out that a simple binary collision cannot explain all the associated tracks.[2]

During the course of photographing cosmic-ray tracks in a magnetic field of 15,000 gauss, one exposure was obtained showing a group of twelve tracks. The tracks, which occurred "early," were coincident in time as shown by the fact that the diffusion of the ions broadened all the tracks to the same extent. The individual ions were clearly resolved.

Seven of the tracks are clearly seen to originate at a common point in the upper portion of the chamber, probably in the wall material. There are in addition five tracks which do not come accurately from this point of origin, but do diverge from the same region of the chamber, their directions perhaps having been changed by scattering

[1] Skobelzyn, Zeits. f. Physik **54**, 686 (1929); Auger and Skobelzyn, C. R. **189**, 55 (1929); Locher, Phys. Rev. **39**, 883 (1932); Millikan and Anderson, Phys. Rev. **40**, 325 (1932); Anderson, Phys. Rev. **41**, 405 (1932).

[2] Millikan and Anderson, reference 1; Anderson, reference 1.

in the chamber wall. In this group while the predominant direction is downward, two are ejected upward.

The sense of curvature in the magnetic field for the seven tracks emanating from the point of origin is such as to indicate electrons. The remainder of the tracks with two exceptions must also be ascribed to electrons on the basis of curvature, range and specific ionization. Protons or heavier particles of the degree of curvature observed would have energies too low to be consistent with the observed minimum ranges and specific ionization. The identification of the remaining particles is not possible. They may be either electrons or protons. The bulk of the tracks, however, and perhaps all represent electrons.

The energies in millions of electron-volts of the measurable tracks are: 35, 33, 32, 30, 20, 17, 17, 14, >30, >10. These energies lie well above the known energies of radioactive processes, and are therefore to be attributed to cosmic rays.

Cosmic-ray ion-chamber experiments have shown occasional bursts of ionization, a million and more ions being apparently formed in the gas of the ion-chamber at one time.[3] Millikan and Neher have observed one burst which seems to correspond to the release of 50 million ions. Obviously electrons cannot be the immediate ionizing agents in producing these large ion-chamber bursts since more than 1000 electrons would have to be assumed to traverse the ion-chamber simultaneously to account for some of them. Heavier nuclear constituents of lower range and greater specific ionization can, however, be called upon to explain the larger effects.

The relation between the burst here described in which most or all the observed particles are electrons, and the large ion-chamber bursts can be determined only through further study.

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Pasadena, California,
February 16, 1933.

[3] Hoffman and Pforte, Phys. Zeits. **31**, 348 (1930). Stienke and Schindler, Naturwiss. **26**, 491 (1932).

The Disintegration of Aluminum by Swiftly Moving Protons

As in our experiments on lithium and boron,[1, 2, 3] we have bombarded aluminum with high velocity protons and have detected, with a Geiger point counter, radiations from the aluminum which penetrate about 8 cm of air. By comparing the absorption of the radiation in mica and aluminum with that in air we eliminated the possibility of an appreciable part of the observed radiation being soft x-rays and proved that particles were being observed. With the scintillation observations of Cockcroft and Walton[4] in mind, we presume the radiation consists of alpha-particles.

The disintegration particles have, as far as we can determine, a continuous distribution of ranges with a preponderance in the lower ranges. Using 1,200,000 volt-protons we observed about 1 particle given off per unit solid angle per 3.6 (10^8) protons having a range in excess of 4 cm while there were only a thirtieth as many with ranges greater than 7 cm. We have found also that the variation in the number of disintegration particles with energy of bombarding protons is the same for all ranges, and that the effective nuclear cross section for disintegration becomes sensibly constant for proton energies above 800,000 volts. In the case of lithium this constancy is reached in the neighborhood of 300,000 volts, while for boron the corresponding voltage is somewhat higher. Thus, for these elements at least it seems that the energy of bombarding protons requisite for nuclear penetration is approximately proportional to the atomic number.

We are grateful for the assistance of the Federal Telegraph Company, the Research Corporation and the Chemical Foundation that has made these experiments possible. We acknowledge also with much pleasure the invaluable assistance of Commander T. Lucci.

M. STANLEY LIVINGSTON
ERNEST O. LAWRENCE

Radiation Laboratory, Department of Physics,
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February 11, 1933

[1] Lawrence, Livingston and White, Phys. Rev. **42**, 151 (1932).

[2] Henderson, Phys. Rev. **43**, 98 (1933).

[3] White and Lawrence, Phys. Rev. **43**, 304 (1933).

[4] Cockcroft and Walton, Proc. Roy. Soc. **A40**, 19 (1932).

PROCEEDINGS
of the
AMERICAN PHYSICAL SOCIETY

MINUTES OF ATLANTIC CITY MEETING, DECEMBER 28–30, 1932

The 34th Annual Meeting (the 182nd regular meeting) of the American Physical Society was held in Atlantic City on Wednesday, Thursday and Friday, December 28, 29 and 30, 1932, in affiliation with Section B—Physics—of the American Association for the Advancement of Science. The presiding officers were Dr. W. F. G. Swann, President of the Society, Dr. Paul D. Foote, Vice-President, Dr. Karl K. Darrow and Professor R. C. Gibbs. There were more than two hundred physicists in attendance at the meetings.

The annual joint session with Section B was held on Thursday morning. The presiding officer was Professor David L. Webster, Vice-President of Section B. The Retiring Vice-President, Professor Bergen Davis, delivered an address on *Conquest of the Physical World* and he was followed by Dr. A. W. Hull of the General Electric Company and Dr. Thomas H. Johnson of the Bartol Research Foundation. Dr. Hull spoke on *Characteristics and Functions of Thyratrons*, and Dr. Johnson on *The Cosmic-Ray Hodoscope and a Circuit for Recording Multiply Coincident Discharges of Geiger-Mueller Counters.*

On Thursday afternoon Professor Richard C. Tolman of the California Institute of Technology delivered the annual Josiah Willard Gibbs Lecture. His subject was *Thermodynamics and Relativity.*

On Friday morning there was a symposium of invited papers on *Cosmic Rays.* The speakers at this symposium were (1) Dr. Gordon L. Locher of the Bartol Research Foundation on *Expansion Chamber Data on Cosmic-Ray Ionization;* (2) Professor R. A. Millikan and Dr. H. Victor Neher of the California Institute of Technology on *New Technique in the Cosmic-Ray Field and Some of the Results Obtained from It,*—Dr. Neher spoke on the new recording cosmic-ray electroscopes which he had developed with Professor Millikan; and (3) Professor Arthur H. Compton of the University of Chicago on *Some Evidence Regarding the Nature of Cosmic Rays.*

The annual dinner of the Society was held on Thursday evening at seven o'clock at the Ambassador Hotel. There were two hundred and nine present. Dr. W. F. G. Swann presided, and introduced the new President, Dr. Paul D. Foote. The after-dinner speakers were Professors Arthur H. Compton, Karl T. Compton, Robert A. Millikan and David L. Webster.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Thursday afternoon, December 29, 1932, in Room 12 of the Municipal Auditorium. The meeting was presided over by President Swann. The President had appointed Messrs. Barton and Breit to canvass the ballots for officers of the Society. They reported the following election for the year 1933:

President	Paul D. Foote
Vice-President	Arthur H. Compton
Secretary	W. L. Severinghaus
Treasurer	George B. Pegram
Members of the Council —four year term	L. O. Grondahl E. C. Kemble
Members of the Board of the Physical Review—three year term	K. K. Darrow J. C. Hubbard A. E. Ruark

The ballots also showed an almost unanimous approval of the following modifications of the constitution which had been recommended by the Council:

Change Article VI, Paragraph 1, to read as follows:

"The President, Vice-President, Secretary, Treasurer, Managing Editor, the three Past-Presidents most recently retired from office, eight other members elected in the manner specified in Article VII, and all Past-Presidents first elected to the office of President prior to December 1932 shall constitute a Council which shall have general charge of the affairs of the Society."

Change Article VII, Paragraph 3, to read as follows:

"No officer of the Society, except the Secretary, Treasurer and Managing Editor, shall be eligible for reelection to the same office until at least one year after the completion of his term of office."

Change Article VII, Paragraph 1, line 6* to read as follows:

"printed on the official ballot. The ballot shall also contain the names of one or more candidates. . . ."

Change Article VII, Paragraph 1, line 9* to read as follows:

"than three weeks before the Annual Meeting. Such a ballot, if marked by a qualified. . . ."

Change Article X†, line 4† to read as follows:

"to all fellows of the Society at least three weeks in advance of the meeting at which such. . . ."

The Secretary reported that during the year there had been 168 elections to membership. The deaths of 20 members have been reported during the year; 50 have resigned. The membership of the Society as of December 28, 1932 is as follows: Members: 1931, Fellows: 667; Honorary Members: 6; Total Membership: 2604.

The Treasurer presented a summary of the financial condition of the Society. It was impossible to present a final report for the year at the Annual Meeting because of the fact that the fiscal year had been changed from ending on November 30th to end on December 31st. The Treasurer's financial report will be audited, presented and distributed.

The Managing Editor made a statement of the condition of the journals of the Society, reporting a deficit of about $3000 as of May 1, 1932 increased at the rate of $750 a month since then. He stated that a thorough study of printing costs and new contracts through the Institute of Physics will make considerable reduction in the cost of publications for 1933. In this connection he referred to the changed format of the journals which would not only result in important economies but will give a double column page which is more easily read and is more adaptable as to set-up than the former single column and rather wide page of the Physical Review. But he stated that the saving will not be enough to enable the Physical Review to continue publishing the same number of pages without incurring a large deficit.

The Editor reported briefly an analysis of the results of the questionnaire which had been sent to members of the Society. Two-thirds of the ten hundred and fifty members replying indicated that they would consider it advisable to discontinue supplying the Physical Review in return for present dues rather than to increase dues, and although a large number of members indicated that they would be willing to pay $2 in addition to dues for membership subscription to the Physical Review the Council had decided that it would be unwise to place any more charges on the members at the present time. The Editor stated that he had therefore only one recourse by which to avoid increasing the deficit on the publications, namely, to reduce the number of pages. He stated that with the cooperation of the contributors he believed that this could be done without materially impairing the publications.

Meeting of the Council. At the meeting of the Council held on Wednesday, December 28, 1932, one candidate was elected to fellowship, three candidates were transferred from membership to fellowship and eighteen were elected to membership. *Elected to Fellowship:* John von Neumann. *Transferred from Membership to Fellowship:* J. E. Lennard-Jones, Gordon L. Locher and Eugen P. Wigner. *Elected to Membership:* Carl O. G. Borelius, L. T. Bourland, S. J. Broadwell, Otis R. Carpenter, Alex de Bretteville, Jr., H. W. Gillett, Helen Staff Hopfield, John J. Hopfield, William Hume II, Charles Lukens, A. M. J. F. Michels, John A. Sanderson, A. F. C. Stevenson, A. Maurice Taylor, John G. Thews, Ancil R.

* Lines are numbered as in Bulletin, Vol. 5, No. 5, Part 2, November 15, 1930.

† As renumbered by action at New Orleans meeting; was formerly Article VIII.

Thomas, Ralph N. Traxler, Glenn M. Webb, Philip S. Williams and R. D. Wyckoff.

The regular scientific program of the Society consisted of 65 papers. Numbers 1, 5, 26, 27, 52 and 60 were read by title. The abstracts of these papers are given in the following pages. An *Author Index* will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Motion of an air-segment in a water-filled capillary tube. WILLIAM SCHRIEVER AND J. F. EVANS, *University of Oklahoma.*—Known pressures were applied to a water column containing an air-segment in a horizontal capillary tube (0.2 mm diameter) and the resulting velocities of the air-segment were measured. A linear relation was found to exist between pressure and velocity, but the experimental curves when extrapolated made small intercepts on the pressure axis. The smallest measurable pressures, however, always produced motion of the bubble. For air-segments longer than a certain length, resistance proved to be independent of the length, but for very short air-segments, the resistance was measurably less. The resistance of an air-segment was shown to be approximately equal to the sum of the resistances offered by its two menisci. The resistance of an air-segment three days old was found to be of the order of ten times as great as that of the same air-segment when fresh. No adequate explanation has been devised for this curious "aging" phenomenon. It was further found that a moving bubble, if suddenly relieved of all pressure, would reverse direction and travel about two-thirds of its own length before stopping. A plausible explanation has been given for this last effect.

2. Physico-mathematical aspects of the conduction of nervous impulse. N. RASHEVSKY, *Westinghouse Research Laboratories, East Pittsburgh, Pa.*—Making the generally accepted assumption, that the propagation of a nervous impulse consists of a continued excitation of adjacent regions by the bio-electric currents produced in the already excited parts of the nerve, we find that the process of propagation is described by an integral equation. As has been shown in a previous publication, the velocity of propagation of such a disturbance is in general not uniform. In the present paper cases are studied, in which this velocity is uniform. Formulae are derived for two different cases. In one it is assumed, that the nerve is electrically homogeneous along its length. In the other, it is assumed that the myelin sheath is a perfect insulator, and that the bio-electric currents can pass only through the Ranvier nodes, where the continuity of that sheath is broken. The theory applies not only to nerve conduction, but formally holds also for the spread of activation in passive metals, such as studied by R. S. Lillie.

3. On a thermodynamic relation in the theory of electrophoresis. O. HALPERN, *New York University.*—The electrokinetic potential cannot in general be subjected to thermodynamic treatment. It is possible however to treat the special case of a particle migrating in a liquid by virtue of adsorbed charged molecules the ionization of which lends itself to thermodynamic discussion. In this way one may explain certain striking regularities connected with electric mobility of dissolved ions and that of surfaces covered with a film of the same ionic material. The same method proves useful in the treatment of colloid stability.

4. Variation with height of convective heat flux from parallel vertical plates. R. B. KENNARD, *Bureau of Standards.*—The temperature distribution between heated parallel vertical plates in air was measured by an optical interference method. Heat loss from the interior surfaces of the plates was calculated from the temperature gradients next to the surfaces, assuming that heat leaves the surfaces by pure conduction in the ambient air. Curves are obtained showing the variation in heat flux from the bottom to the top of the plates. The total convective heat transfer, obtained by integrating these curves, is compared with that obtained directly by electric power measurement, after correcting for radiation. The heat transfer as measured directly is found to be from twenty to thirty percent greater than that calculated from the observed temperature gradients and the accepted value of the conductivity of air. Since no sources of systematic error of this magnitude are suspected, the discrepancy suggests that the effective conductivity of the air near the surfaces may be somewhat greater than that determined under static conditions. The possibility of considerable departure from straight laminar flow in the region very near the plate is considered. An application of the studies to the design of fin type radiators is made.

5. The electrical potential of amorphous and crystalline amphoteric surfaces in liquids. O. WINTERSTEINER AND H. A. ABRAMSON, *Columbia University.*—It has been shown that the ionization of protein molecules adsorbed onto quartz surfaces is not changed appreciably by the adsorption process. That is, the electric mobility of the dissolved protein ions and that of microscopically visible quartz particles covered with an adsorbed film of the protein are practically identical. Insulin is a readily crystallizable protein which is highly insoluble near and at its isoelectric point. The electric mobility of the crystals of this protein has been studied simultaneously with the electric mobility of the amorphous protein (adsorbed or in particle form). The crystal surfaces were negatively charged at the isoelectric point of the amorphous surface. This is interpreted (in harmony with previous data on amino-acid crystals) as evidence for the point of view that at the

extreme limits of the crystal lattice of these amphoteric crystals the polar groups are oriented in such a way as not to be available for ionization in the simple sense found for the adsorbed protein. It is possible to choose conditions so that adsorption of a film of amorphous insulin onto the surface of the crystal itself can be effected, giving the crystalline surface the electrokinetic properties of the surfaces of the dissolved or amorphous, adsorbed material.

6. A potential problem for a semi-infinite medium of variable conductivity. L. B. SLICHTER, *Department of Geology, Mass. Inst. of Technology.*—In determining electrically the depth to bed rock in foundation problems, and in larger scale studies of the upper crust of the earth by electrical means, the problem arises of interpreting a potential field observed at the surface due to a point electrode in terms of the conductivity of the sub-soil. The simplest case is that in which the structure is essentially horizontal so that the conductivity varies only in the vertical direction. The direct problem is not uniquely solvable, but results of sufficient reliability may be obtained by comparing the observed data with corresponding results computed for assumed structures. The postulated structures have always consisted of a number (usually two or three) of discrete layers, each of constant conductivity. The labor of computation is very great when this number exceeds three. This problem is here examined when the conductivity is permitted to vary continuously with depth. Particularly simple solutions exist when the conductivity function consists of a number of straight line segments. Some comparisons between solutions for the layered type of medium and those for the continuously varying type are given.

7. An experimental study of the motion of particles in systems of complex potential distribution. R. D. WYCKOFF AND H. G. BOTSET, *Gulf Research Laboratory, Pittsburgh. (Introduced by P. D. Foote).*—Certain practical problems in the flow of liquids through porous media involve the tracing of the motion of a given line of particles through the flow system. Because of the equivalence of the pressure in a liquid bearing sand to a velocity potential the motion of a liquid particle in a sand is exactly analogous to that of an ion in an electrolytic system. This analogy suggests the use of electrolytic models for tracing the motion of a line of particles in systems of complex potential distribution where the analysis would be difficult or even impossible. By the use of such models solutions have been obtained for systems involving various configurations and shapes of the sources and sinks. The distortions produced in the system by the presence of impermeable barriers located between the sources and sinks may also be observed. In these models the motion of the particles is indicated by a sharp trace representing the line of advance.

8. Interatomic distance calculations for ionic crystals. M. L. HUGGINS AND J. E. MAYER, *Department of Chemistry, Johns Hopkins University.*—By using the Born and Mayer expression (Zeits. f. Physik **75**, 1 (1932)) for the potential energy of an ionic crystal a set of basic ionic "radii" has been calculated. Interatomic distances computed from these radii agree with the experimental values within the probable experimental error, or nearly so, deviations from additivity due to differences in the relative ionic sizes and in the structure type being calculated quantitatively.

9. A new method for calculating molecular vibration frequencies. DONALD H. ANDREWS, V. DEITZ AND S. GOLDHEIM, *Chemistry Department of the Johns Hopkins University.*—When a polyatomic molecule vibrates freely in a single mode of motion it is necessary that each atom in the molecule vibrate with the frequency characteristic of that mode of motion. As a first approximation it may be assumed that each of the atoms vibrates along a straight line in the manner of an ideal harmonic oscillator. One can then calculate the virtual elastic force which would be necessary to produce the oscillation in question. This force must equal the vector sum of the various forces acting on the atom. In solving for the equation of the motion, one can estimate the directions of motion of the atoms from a knowledge of the shape of the molecule and the forces involved. In this step mechanical models are a considerable aid. The vector diagram of the forces on each atom is next set up and solved for the resultant force. The directions of lines of motion are then altered until the resultant forces on the various atoms are just sufficient to give them all the same frequency. It is possible in this way to obtain the modes of motion for a number of molecules too complex to be treated by the ordinary methods. Using the generally accepted values for the force constants it is possible to calculate values of the frequencies which are in good agreement with the observed data.

10. The index of refraction of carbon dioxide as a function of the density. FREDERICK L. BROWN, *University of Va.*—Our present data on the optical properties of gases at high pressures are meager and the theories are conflicting. The method here described is similar to that of Phillips (Proc. Roy. Soc. London, **A97**, 225–240 (1920)). A Fabry-Perot interferometer is completely enclosed in a steel bomb, with heavy glass windows, immersed in a constant temperature bath at 34.1°C. The bomb is connected through a drying tube to a calibrated burette by means of which the total amount of gas is measured by a "bailing out" process. The accompanying fringe shift is obtained by actual count. It was found that the Lorenz-Lorentz function $(\mu^2-1)/[(\mu^2+2)\rho]$ does not remain constant. The inverse of the Lorenz-Lorentz function when plotted against density shows a marked increase at the higher densities. The data included densities in excess of 0.8 g/cc and refractive indices in excess of 1.19.

11. The Raman spectra of five higher alcohols. P. L. BAYLEY, *Lehigh University.*—The Raman spectra of five normal alcohols (amyl to nonyl) have been determined. In the series from methyl through hexyl alcohol the number of Raman lines increases with the length of the carbon chain and the position of the lines show a regular progression. In heptyl, octyl, and nonyl alcohol, however, only those lines corresponding to the spectrum of ethyl alcohol

could be found. Spectra taken of hexyl and heptyl alcohols with equal intensity of both the main lines and the scattered background show the change clearly. This change may be due to the tendency of high boiling point liquids to produce faint and diffuse lines but it is nevertheless surprising that it should occur so sharply. A comparison of spectra of the series of normal alcohols with those of the corresponding iso-compounds shows that the number and relative positions of lines are determined almost entirely by the number of carbon atoms in the chain,—*n*-butyl and iso-amyl alcohols having almost identical spectra and likewise far lower members of the series. The broad line at $\Delta\nu = 1450$ is definitely double in iso-amyl and hexyl alcohols. Hexyl alcohol alone has a line beyond 1450, at 1657A.

12. Attempts to observe an electron affinity spectrum. O. OLDENBERG, *Harvard University.*—The failure of previous attempts to observe an electron affinity spectrum (due to the combination of neutral, electronegative atoms and electrons) is explained by inadequate experimental methods. Based on recent results regarding combination spectra of positive ions and electrons, new attempts have been made to observe the electron affinity spectrum of atomic iodine by using three methods (hollow cathode, positive column with addition of a rare gas, glowing filament). No new spectrum was observed. This failure is discussed theoretically. It seems that the capture of electrons by halogen atoms is an improbable process as compared with the combination of positive ions and electrons.

13. Recombination spectra in the positive column of a caesium discharge. F. L. MOHLER, *Bureau of Standards, Washington.*—Mohler and Boeckner (Bur. Standards J. Research **2**, 489 (1929)), found that the intensity of the caesium recombination spectrum increased with vapor pressure and varied less rapidly with electron concentration than was to be expected on the hypothesis of spontaneous recombination. It has been possible to measure the intensity over a much wider range of conditions by sighting along the axis of a columnar discharge. The intensity distribution between continuous bands and higher series lines remains nearly the same. The intensity at equal electron concentrations is nearly proportional to the vapor pressure. Curves of intensity *versus* electron concentration increase as the square of the concentration with low concentration and become linear at higher concentration. The form of the curves can be explained by assuming that recombination takes place at a rate proportional to the square of the electron concentration and that the radiation is quenched by electron collisions in a process which is the converse of ionization by collision. A similar process has been assumed by Webb and Sinclair (Phys. Rev. **37**, 182 (1931)) to explain the afterglow in mercury though they found that only the electrons with energy exceeding about one volt were effective in quenching mercury radiation.

14. The effect of a small admixture of a foreign gas on the conductivity of a rare gas irradiated by its own resonance radiation. O. S. DUFFENDACK AND R. W. SMITH, *University of Michigan.*—An investigation is made of the effect of impurities on the conductivity produced in Ne and in He at pressures from 1 to 10 mm by irradiation with their own resonance radiation. The conductivity is deduced from the volt-ampere characteristic of neighboring parallel plane collectors placed in the unionized gas between two low-voltage arcs ten tube diameters apart. The characteristic is linear on both sides of the voltage axis and obeys the mobility equation. It is found that for carefully purified gas the conductivity becomes relatively small. It thus appears that under the conditions of these experiments electron emission by impact of metastable atoms with the collector surfaces and tube walls is a negligible factor. Addition of a trace (0.001%) of A or Kr causes a marked increase in conductivity while addition of Ne to He causes a decrease. The explanation is proposed that metastable atoms which are probably formed indirectly through absorption of resonance radiation suffer either ionizing collisions (increased conductivity) or dissipative collisions (decreased conductivity) depending on the ionization potential of the added foreign gas. The work is being extended to permit estimation of collision probabilities and action cross sections.

15. An extension of the Pt I-like isoelectronic sequence to tellurium IV, lead V, and bismuth VI. G. K. SCHOEPFLE, *Cornell University.* (*Introduced by R. C. Gibbs*).—By using a vacuum spectrograph in the region of 657A to 1965A some of the lines arising from the transition d^9p to d^9s electronic configurations of Tl IV, Pb V, and Bi VI have been found. Except for the $^3P_0$ term, the values of the ^3PDF, ^1PDF ($5d^96p$) and ^3D, ^1D ($5d^96s$) are determined with respect to $^3D_3$. These data are compared with those for the ($4d^95p$) to ($4d^95s$) transition of the Pd I-like sequence. Note is taken of the work by Mack, Carroll, Rao and Arvidsson.

16. Pressure broadening of spectral lines. HENRY MARGENAU, *Yale University.*—Pressure broadening by foreign gases has been treated in a previous paper (Phys. Rev. **40**, 387 (1932)) on the basis of a statistical analysis of the van der Waals interaction curves. It is now shown that this statistical analysis must necessarily lead to the same result as the more common, but less perspicuous, procedure of expanding the modulated frequencies in a Fourier integral. There is no collision broadening which is not included in the effect previously discussed. Extending the former results, we have calculated the distribution of frequencies within a spectral line broadened by very high pressures, obtaining an approximate closed expression, and an accurate function which can be evaluated graphically. Agreement with experiment is good, but not entirely unambiguous because of lack of certainty of the molecular constants of attraction. More significant, perhaps, is the fact that it is possible now to determine the latter from an analysis of the line contour.

17. A new band in the spectrum of the OH molecule. HERRICK L. JOHNSTON, DAVID H. DAWSON AND MARGERY

K. WALKER, *Department of Chemistry, The Ohio State University.*—Although the ultraviolet "water vapor" bands were among the earliest molecular spectra to undergo extensive investigation, heretofore only six bands have been reported. These involve transitions between the (0, 1, 2) vibrational levels of an excited $^2\Sigma$ state and the (0, 1) vibrational levels of the normal $^2\Pi$ state. With improved conditions for exciting the spectrum we have obtained 91 lines, heretofore unreported, in the neighborhood of the (0′, 1″) band at λ3428. 44 of these lines prove to be extensions of λ3428; 54 lines (including 11 in common with λ3428) form a new band with a head at λ3484; and 4 lines remain unidentified. Analysis of the new band identifies it as the (1′, 2″) band of the "water vapor" system. A preliminary calculation of the moment of inertia of the new ($V''=2$) level yields 1.625×10^{-40} g cm² as compared with 1.496×10^{-40} and 1.558×10^{-40} for the respective ($V''=0$) and ($V''=1$) levels. The identification of the new band permits the formulation of the vibrational energy equation for the normal $^2\Pi$ electronic state of OH, as $G=3735.0(V+\frac{1}{2})-82.8(V+\frac{1}{2})^2$.

18. The infrared rotation vibration spectrum of hydrogen sulphide. A. D. SPRAGUE AND H. H. NIELSEN, *Ohio State University.*—The fine structure of the hydrogen sulphide band at 1.9μ, first reported by Mischke (Zeits. f. Physik **67**, 106 (1931)), has been explored in absorption with a prism-grating spectrometer by using a grating of 3600 lines per inch and slit widths of 0.2 mm. The absorption cell, thirteen inches long, gave a maximum absorption of about 20% of the incident energy. It was found that the general contour of the band had two maxima which lay at 1.93μ and 1.97μ, respectively. The wave-length at which this band occurs suggested that it might be a harmonic of the band at 3.73μ investigated by Nielsen and Barker (Phys. Rev. **37** (1931)), but this band showed only one maximum. It therefore seemed of interest to reexamine the 3.73μ band with the view of definitely establishing the 1.9μ band as its overtone or not. This examination disclosed that the band reported at 3.73μ was actually only half the whole band, and that the second maximum occurred at about 3.88μ. The spacings between adjacent prominent lines are apparently of the same order as those for the harmonic.

19. Barium hydride band spectra in the near infrared. WILLIAM W. WATSON, *Yale University.*—Two new band systems of the molecule BaH have been found, one in the region of 9000A, the other beyond 10,052A. The first with principal heads at 8924A and 9017A degraded to the red is $^2\Sigma\rightarrow{}^2\Sigma$ with the same lower $^2\Sigma$ as for the $^2\Pi\rightarrow{}^2\Sigma$ bands in the visible red. A quantum analysis gives for the upper $^2\Sigma$ state $B_0=3.232$, $D_0=-1.323\times10^{-4}$ and $\gamma_0=-4.84$. This very large spin doubling indicates strong interaction with a near-lying, lower $^2\Pi$ state. Computation gives 1700 cm^{-1} for the interval $\nu(\Pi, \Sigma)$, and thus this $^2\Pi$ is undoubtedly the upper state for the bands observed beyond 10,052A. The nature of the electron configurations for these four BaH states is discussed. Experience in the use of infrared sensitive plates in photographing emission band spectra is detailed.

20. The production of specified wave forms with the photoelectric siren. HAROLD P. KNAUSS, *Ohio State University.*—If a siren disk is used to interrupt a beam of light falling on a photoelectric cell, the amplified output produces a complex tone similar to that of the familiar air siren. Milne and Fowler (Proc. Roy. Soc. **A98**, 414 (1922)) made a study of the wave form of the Seebeck air siren, and found that they could design orifices for the disk to produce a practically pure tone. In the photoelectric siren, it is easier to make the disk openings of some simple shape, and modify the stationary aperture to produce desired wave forms. The disk used in the present experiments has radial slots 5 degrees wide, spaced at 30 degree intervals. It is placed near a lens which throws an image of a small source of light on the photoelectric cell, and interchangeable stationary apertures are placed between the disk and the lens. Assuming a stationary aperture bounded by an arc of radius r_0, and a curve expressed as $f(\theta)=r-r_0$, the area exposed at any instant will be $A=\int_\theta^{\theta+\pi/36} f(\theta)d\theta$ and the photoelectric current will vary as this integral varies with the time. The function $f(\theta)$ may thus be determined for a given wave form, or *vice versa.*

21. Measurements on contact potential difference between different faces of copper single crystals. H. E. FARNSWORTH AND B. A. ROSE, *Brown University.*—Measurements on contact potential difference between the (111) and (100) faces of single crystals of copper, as a function of the time of outgassing in a high vacuum, were made by the standard Kelvin null method. Care was first taken to obtain smooth surfaces etched parallel to the desired planes with practically no etching parallel to other planes. Two sets of observations with different experimental tubes show that the (111) face assumes a positive potential with respect to the (100) face. This value increases rapidly from near zero to about 0.4 volt during the first few hours of outgassing at dull red heat, and then more slowly to a limiting value of $0.463\pm.002$ at 70 hours and remains constant to at least 150 hours. In one case the value decreased by further heating at temperatures which exposed other faces by evaporation. Observations were taken at a pressure of about 10^{-7} mm Hg as measured on an ionization gauge. Although the present outgassing is not complete it is more than that required to reduce the surface gas layer to such a thickness that it possesses a definite crystal structure related to that of the underlying copper, as shown by Farnsworth. Hence the above result should be characteristic of surface gas crystals on copper.

22. Equivalent circuit of a blocking-layer photo-cell. LAWRENCE A. WOOD, *Cornell University.*—Observations by Schottky and Deutschmann on the cuprous oxide rectifier indicate a circuit consisting of a capacitance and two resistances, probably arranged with one shunting the capacitance and the other in series with the combination.

Capacitance bridge measurements at audiofrequencies with a Weston Photronic Cell indicate that for this a second capacitance element must be added to the previously mentioned circuit. The graph of observed values of effective reactance against effective resistance is a circle with its center displaced from both axes. Displacement of the center from the resistance axis seems to arise only from the addition of a second reactance element. Upon illumination of the cell the radius of the circle decreases and the displacements are diminished. The new values are reached quickly upon illumination, but after illumination require almost ten minutes to return to their original values. Measurements of the varying component of the voltage produced by the cell when illuminated with light of sinusoidally-varying intensity show a rapid decrease with frequency. Resonance may be obtained by placing an inductance across the cell. The relation of these observations to the equivalent circuit of the photo-cell is discussed.

23. Interpretation of x-ray satellites. HUGH C. WOLFE, *Heckscher Research Assistant, Cornell University.*—Druyvestyn's explanation of the $K\alpha$ satellites has been put to the test of numerical calculation by using the Hartree field in the case of potassium ($Z=19$). The $K\alpha$ satellites are attributed to transitions from states with one K and one L electron missing to states with two L electrons missing. By treating e^2/r_{12} as a perturbation and using the wave functions of the unperturbed Hartree wave equation, the energies belonging to the configurations $1s\ 2s$, $1s\ 2p$, $2s\ 2p$, and $(2p)^2$ were calculated according to Slater's theory of complex spectra. The symbols describing the configurations refer to electrons missing from closed shells. The assumption of Russell-Saunders coupling is a justifiable approximation since the interchange energies turn out to be large compared with the spin-orbit interaction, which is measured by the $K\alpha$ doublet separation. There are five allowed transitions which may be correlated with five characteristic $K\alpha$ satellites

Line	ν/R obs.	Transition		ν/R calc.
$K\alpha'$	245.05	$1s\ 2p\ {}^1P \rightarrow (2p)^2\ {}^1S$		245.05
$K\alpha_3$	245.56	$1s\ 2s\ {}^3S \rightarrow 2s\ 2p\ {}^3P$		245.63
$K\alpha_4$	245.69	$1s\ 2s\ {}^1S \rightarrow 2s\ 2p\ {}^1P$		245.53
$K\alpha_5$	——	$1s\ 2p\ {}^3P \rightarrow (2p)^2\ {}^3P$		246.38
$K\alpha_6$	——	$1s\ 2p\ {}^1P \rightarrow (2p)^2\ {}^1D$		246.15

$K\alpha_{5,6}$ are not observed in potassium but appear in other elements as a doublet at higher frequency than $K\alpha_{3,4}$. A small change in the interchange integrals would reverse the sequence of the frequencies calculated for $K\alpha_3$ and $K\alpha_4$ and likewise for $K\alpha_5$ and $K\alpha_6$. The reason for choosing the transitions assigned here is to make $K\alpha_3$ and $K\alpha_5$ appear as triplet-triplet transitions, since these lines have fine structure. The strong lines, $K\alpha_{3,4}$, which persist from $Z=11$ to $Z=30$, are due to an initial $KL(2_1)$ ionization. The weak lines, $K\alpha'$ and $K\alpha_{5,6}$, which appear from $Z=11$ only to $Z=19$ and $Z=16$, are due to an initial $KL(2_2)$ ionization.

24. A critical study of the intensity formula for the powder method of crystal analysis. F. C. BLAKE, *Ohio State University.*—By combining the Thomson and Lorentz factors into a single factor, and the usual structure factor and the atomic form factor into another single factor, the intensity formula consists of the product of these two together with the form or multiplicity factor, the Debye temperature factor and the absorption factor, treated by Claassen and Rusterholz. It is possible from a knowledge of these five factors to study intensity as a function of the wave-length for metals of different atomic numbers. Calculated results can be compared with experiments by means of densitometer experiments properly interpreted. The comparison has been made for aluminum using molybdenum and copper rays and agreement found for molybdenum rays. The reasons for disagreement when copper rays are used are discussed. There are other factors not properly handled in the intensity formula. These are discussed.

25. α-particles from ionization chamber materials. J. A. BEARDEN, *Johns Hopkins University.*—The troublesome effect of α-particles in the measurement of small ionization currents is well known. The number of α-particles emitted by various materials usually used in ionization chambers has been determined by using an F P 54 vacuum tube and photographic recording over long time intervals. It was found that cold rolled steel was the best material for the walls and electrodes of chamber. Brass and copper were the next best materials. Careful cleaning of the metal surfaces with sandpaper reduced the number of particles usually observed by about 75 percent. Such a cleaned surface when exposed to air for a few hours returned almost to its original condition. Iron under the best conditions gave less than 3 α-particles of range greater than 4 mm per 100 sq. cm per hour. Attempts were made to purify copper and use plated surfaces, but this was not successful. Thin celluloid, painted with india ink or thin iron foil was found satisfactory for windows. However some samples of india ink were not satisfactory. Well cleaned amber was very good for an insulator, while glass was poor. Methyl bromide, good quality CO_2, and N_2 were found to be suitable gases.

26. New electron diffraction rings in zinc oxide and their interpretation. K. LARK-HOROVITZ AND H. J. YEARIAN, *Purdue University.*—The diffraction of zinc oxide powder deposited from an electric arc between zinc electrodes has been investigated with electrons from 6 to 20 kv velocity. Besides the ordinary diffraction rings corresponding to the x-ray pattern, diffraction rings have been observed corresponding to 1/2 of 100 and 1/2 of 002.

Voltage.....	19500	16700
Ratio of diameters..	D_1/D_{100} 0.482	
	D_2/D_{002} 0.498	0.501

These rings are of much smaller intensity than the ordinary diffraction rings. The diameter of these rings as obtained for different voltages agrees with the value calculated for the different wave-lengths. Assuming that besides the diffraction from solidly packed crystallites ($n\lambda = 2d \sin \theta$) diffraction also occurs from loosely arranged crystallites, in

which case refraction at the surface of each crystallite takes place $n\lambda(1-(4d^2/150n^2)V_0)^{1/2}=2d\sin\theta$ where d is the spacing, n the order of diffraction and V_0 the inner potential of the crystal these rings can be interpreted using an inner potential of 4 volts for zinc oxide. The rings appear strongly if the powder shows a mesh of loosely arranged fibers under the microscope, and while these fibers break after continued electron bombardment, the rings become weaker in agreement with the explanation given above.

27. The problem of the intrinsic magnetic field by P. Weiss. JAKOB KUNZ, *University of Illinois.*—A large number of magnetic phenomena have been coordinated by P. Weiss by the assumption of an intramolecular magnetic field. On the other hand arguments have been advanced by Akulow and Honda against the existence of such a field of 6 to 14,000,000 gauss. The strongest argument of Weiss consisted in the calculation of the increase of the specific heat of the ferromagnetic materials in the neighborhood of the Curie point. But the phenomena of the specific heat above the Curie point are not accounted for in Weiss' theory. Moreover it has recently been found that there exists in magnetite a sharp increase of the specific heat and a sudden change in the magnetic properties far away from the Curie point, and other substances such as paramagnetic MnO also show a very abrupt change of the specific heat at a low temperature. The magnetocaloric effect determined by $dT=-(T/C_4)(dJ/dT)dH$ is given by thermodynamics alone. The transition of ferromagnetic into paramagnetic properties is, especially in Weiss theory, obscure, as the number of magnetons is very different below and above the Curie point.

28. The dynamic aspect of ferromagnetism. F. BITTER, *Research Laboratories, Westinghouse Elec. & Mfg. Co., East Pittsburgh.*—During the last few years a static theory of ferromagnetism has been achieving considerable success. In its latest form this theory expresses the energy of a crystal as a function of the direction of magnetization as follows:

$$E_\theta=c\Sigma^1\alpha_i^2\alpha_j^2+k_1\Sigma A_{ii}\alpha_i^2+k_2\Sigma^1 A_{ij}\alpha_i\alpha_j-I_w\Sigma H_i\alpha_i+\text{const}$$

and claims that the actual direction of magnetization is given by the direction in which E_θ has a minimum. A_{ij} are the components of the strain tensor describing the distortion of the crystal, and α_i etc. are the direction cosines of I_w. The summations are with respect to i, j, k. In order to apply such a static theory consistently we should seek the minima of E_θ not under constant strain, but under constant stress. The stress tensor components are given by $F_{ii}=\partial W/\partial A_{ii}$ etc. We assume this differentiation to be carried out with α_i etc. constant.

$$W=\frac{c_{11}}{2}\Sigma A_{ii}^2+\frac{c_{12}}{2}\Sigma^1 A_{ii}A_{jj}+c_{44}\Sigma^1 A_{ij}^2+E_\theta$$

c_{11}, c_{12} and c_{44} are elastic constants. With the help of these expressions we may write A_{ij} as a linear function of the quantities F_{ij}. Substituting in the expression for W we obtain

$$E_\theta^1=c^1\Sigma^1\alpha_i^2\alpha_j^2+k_1^1\Sigma F_{ii}\alpha_i^2+k_2^1\Sigma^1 F_{ij}\alpha_i\alpha_j-I_w\Sigma H_i\alpha_i+\text{const.}$$

All terms not involving α are lumped in the final constant. The new coefficients have the values

$$c^1=\frac{k_1^2}{2(c_{11}-c_{12})}-\frac{k_2^2}{4c_{44}}+c;\qquad k_1^1=0;\qquad k_2^1=0.$$

Accordingly, all terms involving products of F and α drop out of W. This static theory of ferromagnetism predicts that magnetization is unaffected by externally applied stresses, in contradiction to experimental facts. The correct theory is probably a dynamic one in which I_w oscillates so rapidly that the quantities A_{ij} remain constant because of the large inertial forces acting on the heavy nuclei.

29. The temperature dependence of Young's modulus for nickel. JERROLD ZACHARIAS, *Columbia University.*—Young's modulus is calculated from the free period of longitudinal vibration of a thin rod. The latter is found experimentally for temperatures between 30°C and 400°C by a method previously described (S. L. Quimby, Phys. Rev. 39, 345 (1932)). Observations are here reported upon single crystals grown from especially pure nickel and upon hard drawn, polycrystalline rods of commercial nickel which contained copper, carbon, iron, manganese, silicon and cobalt to the amount of 1.1 percent. The variation of Young's modulus with temperature depends on the previous thermal history of the sample. Between 30°C and 200°C Young's modulus for *annealed* specimens decreases about 13 percent. This is followed by an increase to the Curie point of about 6 percent and above the Curie point by a linear decrease. For single crystals the maximum at the Curie point is so sharp as to indicate a discontinuity in the temperature coefficient. For *hard drawn* specimens and specimens *quenched* at 1100°C the minimum is wholly absent. Young's modulus decreases continuously to the Curie point, where, however, the temperature coefficient suffers an abrupt change.

30. A magnetic velocity selector for molecular beams. I. I. RABI AND V. W. COHEN, *Columbia University.*—In experiments on the direct measurement of nuclear spin by magnetic deflection of molecular beams it was found convenient to use a magnetic velocity selector. A portion of a beam of neutral sodium atoms, spread out in a velocity spectrum by an inhomogeneous magnetic field, is selected by a movable selector slit for further analysis. Beams 53 cm long and velocities 1/2 the average for the corresponding temperature have been used. For a given width of selector slit resolution varies inversely as the selected velocity. The beam was detected with the Langmuir-Taylor surface ionization detector. An original beam intensity of 30 cm, galvanometer sensitivity 1 mm $=10^{-12}$ amperes is reduced to 1/300 by the selector with a resolution $dv/v=1/10$. Detector fluctuations are of this order. However, we found it possible to accumulate sodium for 8 minutes on the cold detector wire. By sudden heating we obtain 15 cm ballistic throws corresponding to complete ionization of the accumulated sodium. Residual gases and impurities give no appreciable effect. With the accumu-

lation method it was relatively simple to perform further experiments with the very feeble monochromatic beam.

31. Direct measurement of the scattering of potassium atoms by other atoms and molecules. W. H. MAIS AND I. I. RABI, *Columbia University.*—A narrow beam of neutral potassium atoms (angular width 20′) was scattered by hydrogen, helium, nitrogen and carbon dioxide under low pressure. The scattering was investigated by means of a surface ionization detector, as a function of angle with the original beam from 0° to 60°, as a function of pressure of the scattering gas, and of the temperature of the potassium beam. The results allow a determination of the scattering function or f curve within these limits. The small angle scattering expressed in terms of collision radii gives much larger collision radii than either kinetic theory radii or radii obtained from lattice distances. However, if one defines as a collision a change of direction of the potassium atoms of one-half degree, then the computed radii approach more closely the values to be expected. For the temperature of the potassium atoms the de Broglie wave-length is of the order of 2×10^{-9} cm and we consequently would hardly expect any contribution to the scattering of the potassium atoms due to diffraction by the scattering gas atoms. The results may therefore allow of an evaluation of the mutual interaction between the potassium atoms and the atoms of the scattering gas.

32. Orthogonality of scattered-wave functions. E. H. KENNARD, *Cornell University.*—Solutions of the equation, $\Delta\psi+a^2(W-V)\psi=0$ are sometimes needed which at infinity take on the form $\psi=e^{i\mu\cdot\mathbf{x}}+\Phi$, $\Phi\sim Ce^{i\mu r}/r$; cf. the functions used in treating x-ray emission by Sommerfeld, who proved their orthogonality in that case by a special argument. A general proof that such solutions are always orthogonal when V is suitably restricted to the neighborhood of a point P can be arrived at by paraphrasing mathematically the following argument. Let two wave packets with almost-definite energies approach P in different directions from infinity. In the beginning they do not overlap ($\Phi=0$) and so are obviously orthogonal; in consequence of the Schrödinger time equation they preserve this orthogonality; then as they flow over P the diverging Φ waves develop and ψ becomes in each packet approximately a characteristic solution of the type in question. For a convenient mathematical statement one writes down

$$I=\int e^{-i\beta\mu_1^2}(e^{-i\mu_1\cdot\mathbf{x}}+\Phi^*(\mu_1))d\tau\int_{\delta\pi}e^{i\beta\mu^2}(e^{i\mu\cdot\mathbf{x}}+\Phi(\mu))d\pi,$$

$\delta\pi$=any region in the μ space; one then shows that $dI/d\beta=0$, and that as $\beta\to\infty$ the contributions from Φ to I vanish and by Fourier integral theory $I=0$ unless μ_1 lies in $\delta\pi$. It follows that $I=0$ when $\beta=0$, which expresses the desired orthogonality.

33. The probability function for the production of He^{++} by single electron impact. WALKER BLEAKNEY, *Princeton University.*—With a mass-spectrograph previously described (Phys. Rev. **40**, 496 (1932)) the He^{++} ion was found as a result of single electron impact. The ionization potential turned out to be 79 volts as expected. Above this point the effective cross section for such a collision increases rapidly with increasing electron velocity and passes through a maximum in the neighborhood of 330 volts. At this point the effective cross section is of the order of 2×10^{-19} cm². It is concluded therefore that of all the helium ions produced by 330-volt electrons about one percent are originally doubly charged. At higher electron velocities the relative number increases slightly but the actual number decreases.

34. Measurement of the masses of He and H^1, Ne^{20}, Ne^{22}, B^{11}, Cl^{35} and Cl^{37} with a mass-spectrograph. K. T. BAINBRIDGE, *Bartol Research Foundation of the Franklin Institute, Swarthmore, Pa.*—The ratio of the masses of He and H^1 was measured by comparison of He^{++} and H_2^{1+} on fourteen spectra. Referred to $H^1=1.00778$, $He=4.00218\pm0.00004$. All of the succeeding masses are referred to O^{16}. $Ne^{20}=19.9967\pm0.0009$ from ten spectra by measurement of the Ne^{20} line with respect to the known masses of C and O hydrides, and C_2 and its hydrides. $Ne^{22}=21.99473\pm0.00088$ from five spectra by measurement of Ne^{++} in relation to C^+ and its hydrides over the linear part of the mass scale. Both neon values are outside Aston's limit of error and an explanation for his extraordinarily high mass values will be suggested. Within the limits of error of the Ne^{22} and F^{19} masses, the mass of Ne^{22} is in agreement with the mass calculated from the disintegration experiments on F^{19}. $B^{11}=11.01073$ from two spectra as determined by the same method used for doubly ionized Ne^{22}. Cl^{35} and Cl^{37} were measured in the second order (doubly ionized) by comparison with OH, OH_2, OH_3 ions. $Cl^{35}=34.9796\pm0.0012$ from seven spectra, and $Cl^{37}=36.9777\pm0.0019$ from five spectra. Sample spectra will be shown.

35. Decay of luminescence and light absorption in phosphorescent materials. D. H. KABAKJIAN, *University of Pennsylvania.*—A number of substances were exposed to alpha, beta and gamma-rays from radium or polonium and the variation in their light absorption coefficient, μ, was determined. The substances were either in the form of transparent plates or of deposits of crystalline powder on thin glass. The rate of variation of μ for all the substances investigated, whether phosphorescent or non-phosphorescent, can be represented by curves of the same type. It is found that for a constant source of radiation μ does not increase exponentially with time but tends to reach a saturation value. The saturation value for each material depends upon the intensity of the irradiation but is independent of the total amount of energy absorbed by it. It also depends upon the temperature at which irradiation takes place. The increase in the value of μ does not seem to be directly related to the light emissivity of the material. With the data obtained from the absorption curves it is possible to plot luminous flux-time curves of irradiated phosphorescent materials instead of brightness-decay curves. The curves show a decay of flux that can not be represented by a simple exponential.

36. Fluorescence of solutions of chlorophyll *a*. H. V. KNORR AND V. M. ALBERS, *Kettering Foundation, Antioch College.*—The fluorescence of chlorophyll *a* in solution in anhydrous ether, benzene, acetone and methanol has been photographed by means of a Hilger E_3 spectrograph. The fluorescence was excited by radiation from four Pyrex mercury arcs. The solutions were maintained at a temperature of 6° centigrade. One minute exposures on Ilford hypersensitive panchromatic plates were used to obtain the spectrograms. The concentrations used were 1 mg per 100 cc of solution. The fluoresence consists of a main band, the wave-lengths of its maximum being 6718A for ether, 6767A for benzene, 6720A for acetone and 6745A for methanol; a second band the wave-length of its maximum being 6330A for ether, 6358A for benzene and 6392A for acetone. A shift in the position of the main band toward the violet and the second band toward the red is observed when the solutions are irradiated continuously. This shift is attributed to additional bands of the new fluorescent compounds which are formed photochemically. The initial positions of these bands do not agree with those observed by earlier investigators. Two additional bands at 7335A and 6792A have been observed for chlorophyll *a* in ether, by using longer exposures on Eastman extreme red plates.

37. The fluorescence of some substances containing vitamin A. JAY W. WOODROW AND A. R. SCHMIDT, *Iowa State College.*—One of us has previously reported the observation of a fluorescence band at about 550 mμ for cod-liver oil when irradiated by ultraviolet light. With improved equipment, we have obtained two distinct fluorescent bands for cod-liver oil, one a narrow band extending from about 530 to 570 mμ and the other much wider and extending from about 410 to 510 mμ. The same two bands were obtained with butter fat, but they were not so intense. This broad band from 410 to 510 mμ was also obtained with spinach and tomato juice, both of which contain vitamin A. The broad fluorescence band in cod-liver oil is very much reduced in intensity for cod-liver oil which has lost most of its vitamin A potency is due to bubbling air through it at a high temperature. Apparently, the fluorescence is connected with either the vitamin A or the carotin present.

38. "Conquest of the Physical World."* Address of the Retiring Vice President of Section B—A.A.A.S.,

BERGEN DAVIS

Columbia University

The natural impulse of mankind is to obey the command to "Subdue the Earth and have dominion over it." The scientist subdues the forces of nature to beneficent uses. The great mass of mankind has overrun the surface of the earth with irreversible destruction. The conquests of science are a ceaseless adventure, more thrilling than the prosaic adventures of exploration or adventures in the political life. A rapid survey is made of the conquests of physical science, such as the conquests of the heavens, the discovery of the laws of motion by Galileo and Newton, the conservation of mass and the conservation of energy, the establishment of the atomic hypothesis and the electromagnetic theory of light. Two major discoveries at the close of the last century were the Roentgen rays and radioactivity. These initiated the study of the structure of matter and the nuclear atom of Rutherford and Bohr. The quantum theory of radiation, and its absorption and emission rapidly followed. The special relativity theory of Einstein was a major conquest, containing the broad generalization of the identity of matter and energy. Studies in radioactivity and the photoelectric effect definitely established that matter and energy are atomistic. There is no continuum in nature. The discovery of isotopes, together with the identification of matter and energy led to processes of atomic disintegration and atom building. Recent experiments show that the proton has great chemical affinity for certain atomic nuclei. We are at the beginning of a new chemistry, the chemistry of the nucleus. The way is open that will lead to the conquest of the internal energy of atoms to our uses. The oasis of knowledge has been greatly enlarged, but the surrounding desert of the unknown is still without limit.

* Invited papers.

39. "Characteristics and Functions of Thyratrons."*

A. W. HULL

Research Laboratory, General Electric Company, Schenectady, New York

The fundamental properties of Thyratrons are described and illustrated. Present models are discussed from the standpoint of grid control characteristics, power amplification, starting time, deionization time, current and voltage limits, and efficiency. Typical applications are described to illustrate the different functions which the Thyratron is adapted to serve. These functions include on-and-off control operations, continuous variation of current by phase control, rectification, inversion, frequency changing and commutation of motors. Scientific applications are discussed, and future possibilities briefly forecast.

40. "The Cosmic-Ray Hodoscope and a Circuit for Recording Multiply Coincident Discharges of Geiger-Mueller Counters."*

THOMAS H. JOHNSON

The Bartol Research Foundation of the Franklin Institute

The cosmic-ray hodoscope was designed to provide a continuously sensitive method for tracing the paths of the cosmic rays throughout an extended volume. The present model consists of a bank of 36 counter tubes each of which is connected to a neon flash lamp. The cosmic-ray tracks appear as a row of simultaneously flashing lamps. The method of eliminating flashes other than those due to cosmic rays and the method of recording the flashes are described and possible uses indicated. The circuit for recording coincident counter discharges, designed in collaboration with J. C. Street, is described

and discussed as regards its resolving time, sensitivity and constancy. The paper was illustrated by demonstrations.

41. High-speed ions of stellar origin. Ross Gunn, *Naval Research Laboratory, Bellevue, D. C.*—It is noted that the observed state of rest of numerous ionized calcium clouds guarantees that all interstellar space is substantially neutral. The presence in the solar atmosphere of strong electric fields suggests that negative ions might be accelerated and move off into space with energies of some millions of volts. The process of emission is studied. It is found that only within a sunspot are conditions such that a negative ion can traverse the solar atmosphere and acquire energy comparable to the potential difference between the sun proper and free space. An electron or negative ion which succeeds in traversing the layer emerges at high speed and attracts to itself, from the high atmosphere, a neutralizing positive ion by electrostatic attraction; and, finally, the two ions, forming a neutral pair, leave the sun at precisely the same velocity. The energy of the neutral stream is estimated to be a very small but appreciable fraction of the energy radiated by the sunspot. *Bearing on the penetrating radiation.* Neutral ion pairs of solar origin can have no relation to the penetrating radiation because of their low energy, but similar processes in early type stars will give rise to neutral ion pairs of approximately 10^{10} or 10^{11} electron-volt energies. It is suggested that these energetic neutral ion pairs which perhaps get separated by electromagnetic forces or by collisions in the earth's atmosphere are identical with the penetrating radiation. Reasons are given for believing that the distribution of such particles in space is nearly uniform.

42. The disintegration of lithium by protons of high energy. M. C. Henderson, *University of California.*—The results recently obtained by Lawrence, Livingston and White have been extended to protons having an energy up to 1,125,000 electron-volts. After the rapid increase found by Cockroft and Walton at lower voltages the number of disintegrations per proton increases above 400,000 electron-volts proportionally to the 3/2 power of the energy. The range of the proton is known to be proportional to the same power of the energy. These facts indicate that the probability of disintegration of the individual lithium nucleus is independent of the energy of the proton above 400,000 volts. The relative number of disintegrations over the whole range from zero to 1,125,000 electron-volts is given quite exactly by $N=k'Ve^{-a/V^{\frac{1}{2}}}$ where V is the energy of the protons and k' and a are constants. From 400,000 to the upper limit reached this formula is practically indistinguishable from $N=k(V^{3/4}-V_0^{3/2})$ when the experimentally determined values of the constants are used. The more complex formula has theoretical justification and the radius of the lithium nucleus as calculated from the experimental value of a is about 4×10^{-13} cm. The cross section effective for disintegration seems to be much smaller, with a radius of 1.4×10^{-14} cm. The actual number of disintegrations is half the number of alpha-particles emitted and is equal to 2.0 disintegrations per 10^9 protons at 250,000 electron-volts; 10.2 disintegrations per 10^9 protons at 500,000 electron-volts; 40 disintegrations per 10^9 protons at 1,000,000 electron-volts. The results at 500,000 volts are in excellent agreement with those of Cockroft and Walton. The form of the curve differs slightly and the probable causes of this difference are discussed.

43. The disintegration of lithium by protons. J. R. Oppenheimer, *Berkeley, California.*—The disintegration of lithium by protons first observed by Cockroft and Walton was expected on theoretical grounds; but the disintegration of much heavier elements, which is also observed experimentally, appears irreconcilable with the usual nuclear model. To see whether the voltage dependence of the effect in lithium was in detail in accord with the theory, we have therefore made the calculations, using for model the Gamow model of a repulsive Coulomb potential broken off at a radius r, assuming that the number of capture-disintegrations is proportional to the probability of finding a proton inside r, and taking into account the stopping of the protons in the target. For the range in question the theoretical dependence of the yield on the proton voltage V is given with sufficient accuracy by $V\exp(-aV^{-\frac{1}{2}})$ where $a=2.4\times10^3[1-6(10^{12}r)^3]$. With $a=1930$, this fits all the observations from 1.5×10^5 up to 1.16×10^6 volts within experimental error; in this range the yield varies by a factor of over a hundred. The experimental a gives an $r=3.2\times10^{-13}$, which is small but not impossible. The observed yield is never more than a tenth of the theoretical upper limit, which we get by assuming that every proton which penetrates inside of r causes a disintegration. Thus the present evidence confirms, in the case of lithium, the applicability of the Gamow model.

44. Detection of corpuscular radiation by vacuum tube methods. John R. Dunning, *Columbia University.*—The advantages of the direct detection of the ionization produced by alpha-particles or high-speed protons include linearity, high resolution, freedom from beta and gamma-disturbances, uniform response over large area, adaptability to differential methods, low "natural count," and full quantitative results. This paper is a study of the design of high gain resistance-capacity coupled amplifiers for this purpose. The magnitude and wave form of the initial pulse are functions of a number of factors, and to secure both high sensitivity and resolution, the initial circuits must have special characteristics involving certain compromises. The resistive and capacitative components of the input admittance are highly important, and the reduction of the effective input capacitance associated with the first tube and ionization chamber is discussed. Numerous sources contribute to the noise level which a high initial amplification and other practices minimize. Various types of input tubes have been tested, and the characteristics of an ideal tube are indicated. The complete set-up includes a linear amplifier with staggered time constants, peaked frequency response, isolation filter circuits, extreme shielding, and a balanced output circuit feeding a high-frequency moving light beam oscillograph. The apparatus has been used to obtain oscillograph records of alpha-particles and of protons, both from nuclear disintegration and from neutron impacts.

45. The airplane method of obtaining cosmic-ray intensity data. LYNN G. HOWELL, *Humble Oil Company, Houston, Texas and* LEWIS M. MOTT-SMITH, *The Rice Institute, Houston, Texas.*—In order to obtain new data on the intensity curve of the cosmic radiation at high elevations an airplane was used to carry an electroscope to the various altitudes up to about 27,000 feet. The advantages of this method are discussed. The construction of a high pressure Wulf-type electroscope for this purpose is described. The details of the calibration of the instrument and the technique for making reliable intensity measurements in an airplane are presented. In the course of this work measurements were made at various altitudes of the cosmic-ray absorption by lead shields of thickness 1.3, 2.5 and 4.7 cm. The results of these measurements indicate that there are difficulties in the way of making the corrections for local radiation by the use of shields.

46. Airplane cosmic-ray intensity measurements. LEWIS M. MOTT-SMITH, *The Rice Institute, Houston, Texas and* LYNN G. HOWELL, *The Humble Oil Company, Houston, Texas.*—With the help of the United States Air Corps and particularly of Captain A. W. Stevens of Wright Field the following cosmic-ray measurements have been made: (1) daytime intensity curve from 1000 to 27,000 feet, (2) night-time intensity curve up to 27,000 feet, (3) absorption in a few cm of lead at various elevations, (4) intensity measurement at 27,000 feet during the solar eclipse of August 31, 1932. Comparison with the earlier high altitude measurements, notably those of Kolhörster, indicates that the present curve is steeper at 27,000 feet, so that the marked decrease in the absorption coefficient above 20,000 feet is not observed. It is found, however, that the values at the highest altitudes are too small by a factor of about two to fall on Millikan and Cameron's synthetic cosmic-ray curve. No significant decrease in intensity was observed during the night-time observation even at the highest altitudes. In accord with all previous eclipse measurements, no change in intensity was observed during the solar eclipse.

47. Energy-loss and scattering of cosmic-ray particles. CARL D. ANDERSON, *California Institute of Technology.*—Cloud-chamber photographs of cosmic-ray particles traversing a lead diaphragm of 11 mm thickness taken in a uniform magnetic field of 15,000 gauss have yielded the following facts. Electrons of initial energy of 300 million volts were found to lose about about 35 million volts energy per cm of lead traversed. The mean change in direction due to scattering in the 11 mm lead plate for a group of 33 tracks of $Hr > 10^6$ gauss cm (measured both above and below the lead plate) was 0.7 degrees, the smallest angle being less than 0.2 degrees and the largest 3.1 degrees, the angle being measured in the plane of the front glass plate of the cloud-chamber. This group of tracks represents either (1) electrons of minimum energy 300 million volts, or (2) protons of minimum energy 150 million before traversing the lead plate. For protons the minimum energy based on curvature is 50 million volts, but allowing for the energy loss to be expected in traversing the lead, a lower limit of 150 million volts must be assigned. A second group of 14 tracks comprised of electrons of energies ranging from 100–300 million volts showed a mean change in direction due to scattering in the lead plate of 4.9 degrees, the smallest angle being less than 0.5 degrees and the largest 14 degrees. In general the change in direction in the lead diaphragm due to scattering is much greater than that due to the effect of the 15,000 gauss field.

48. The variation of cosmic-ray intensities with azimuth on Mt. Washington, N. H. THOMAS H. JOHNSON, *The Bartol Research Foundation of the Franklin Institute and* J. C. STREET, *Harvard University.*—The triple coincidence counting rates of three G.M. counters in line were recorded at the elevation 6288 ft. in the four azimuths, magnetic N, S, E, and W with the line of counters inclined 20°, 30°, and 40° from the vertical. For each inclination the lowest counting rate was found in the east, with the west and the north higher than the average. The magnitude of the variations are such that it is exceedingly improbable that they arise from statistical fluctuations. The variations observed in the data for each position are, however, within statistical expectation. An east minimum can be explained on the basis of Störmer's theory of the motion of a charged particle in the earth's field if a preponderance of the cosmic rays observed at that elevation are protons of energies of the order of 10^{10} volts. The absence of an east-west difference at lower elevations would find its interpretation in the idea that the rays which penetrate the atmosphere have energies so high that they are not excluded from the east by the earth's field. It may be also possible to explain the effect by the influence of the earth's field on secondary rays.

49. "Expansion Chamber Data on Cosmic-Ray Ionization."*

GORDON L. LOCHER

National Research Fellow, at the Bartol Research Foundation of The Franklin Institute

Experimental evidence is presented for a new process of ionization by swiftly moving corpuscles. According to this theory, part of the ionization is produced by characteristic x-radiation generated in the gas by the passage of the particle through it. A discussion will be given of the amount of ionization along cloud tracks of cosmic-ray particles, as compared with that found in ionization chambers, also of the rate of influx of the particles, as found with a precision cloud machine and Geiger-Müller counters. An analysis is made of simultaneous groups of cloud tracks.

50. "New Technique in the Cosmic-Ray Field and Some of the Results Obtained with It."*

R. A. MILLIKAN AND H. VICTOR NEHER

California Institute of Technology

There have been developed new types of cosmic-ray electroscopes which are at least ten times as sensitive as the most sensitive of those heretofore used by either of us, and which are in addition self-recording and independent of gravity as well as of the vibrations of the supporting platform. They

* Invited papers.

make a permanent record of cosmic-ray intensities in the localities through which they pass, and a record which is just as accurate and dependable whether the recording instrument is in a moving railway train, automobile, airplane, or steamship, or at rest in a laboratory, so that when a given area has once been surveyed with their aid subsequent students need only come and read their records, permanently preserved on films,—records which are of course entirely free from all personal equation and preconception. These electroscopes have thus far failed to reveal any variation in the cosmic-ray intensities in any of the localities through which they have been carried over the earth's surface so long as they have been kept at a uniform depth beneath the top of the atmosphere. This statement applies accurately to sea-level observations, which have now been carried from 49° north to 8° north. Readings at high altitudes are not yet complete. Also readings with these electroscopes both at low and at high levels (14,000 feet) reveal no direct effect of the sun or of any other celestial objects. Thus far, then, the new technique has brought no evidence that the incident cosmic-ray photons are mixed in appreciable amount with their secondary corpuscular radiations when they enter the atmosphere. The continuation of these readings in the higher atmospheric levels will reveal whether the softer components of the incoming cosmic rays are as free from such mixing as are the harder components.

51. "Some Evidence Regarding the Nature of Cosmic Rays."*

ARTHUR H. COMPTON
The University of Chicago

Five methods of distinguishing between photons and electrons or other charged particles as the primary cosmic rays are discussed: (1) A study of cosmic-ray absorption, which indicates that if electrically charged the rays must have much higher energy than if they are neutral. (2) The intensity at high altitude, which is consistent with the view that charged particles enter the atmosphere from above. (3) The Bothe-Kohlhorster experiment, indicating that high-speed particles exist whose absorption is about that of cosmic rays. (4) Deflection by magnets, which shows electrically charged primary or secondary particles of very high energy. And (5) variations in cosmic-ray intensity with differences in magnetic latitude on the earth's surface. Evidence is presented to show that this difference cannot be due to magnetic effects on secondary electrons, but that it is the primary rays which are thus affected. This supports the view that cosmic rays are electrified particles, with energies (if electrons) of 10^{10} electron-volts and more.

52. A portable high tension voltmeter. H. T. CLARK, *Purdue University.*—A glass tube two inches in diameter and eight inches long is filled with oil and contains two disks and a very light aluminum vane suspended midway between the electrodes. This vane is fixed rigidly to a mirror which is mounted above the oil level (in a side tube) and the assembly suspended on a light gold wire under tension. A potential a.c., when applied to the electrodes, causes a deflection of the vane. The arrangement in oil permits the application of high voltages and furnishes a convenient method of damping. A laboratory model punctured at approximately 120,000 volts. This model has been calibrated up to 25,000 volts for an electrode separation of 6.5 cm. The sensitivity at low voltages is about 100 volts per cm and at high voltages it is about 250 volts per cm for a 1.5 meter scale distance.

53. The electrostatic generation of high voltages for nuclear investigations. R. J. VAN DE GRAAFF, K. T. COMPTON AND L. C. VAN ATTA, *Massachusetts Institute of Technology.*—A previous abstract (Phys. Rev. **38**, 1919 (1931)) described an electrostatic generator consisting essentially of a pair of hollow spherical electrodes charged by belts. Both theoretical and experimental aspects of this type of electrostatic machine will be discussed. A description will be given of the design of a much larger generator now under construction at the M.I.T. experiment station on the Round Hill estate of Colonel E. H. R. Green. The electrodes of this machine are hollow aluminum spheres 15 feet in diameter, the interiors of which afford laboratory space for the operators. Each electrode is mounted on an insulating column of Textolite six feet in diameter and 24 feet high, within which the charging belts run in warm dry air. The machine is designed to develop a steady d.c. potential of the order of 10 million volts with a continuous power output of about 20 kilowatts. If desired this power can be greatly increased by the installation of additional belts. The construction of this machine is well advanced and its operation is expected within a few months. This development was made possible by a grant from the Research Corporation which has also aided effectively in preparing the engineering design.

54. A 1,500,000 volt portable electrostatic generator of rugged design. E. H. BRAMHALL AND R. J. VAN DE GRAAFF, *Massachusetts Institute of Technology.*—For many purposes a compact and portable source of high voltage is needed. To provide for such a demand an electrostatic generator has been constructed developing a constant potential of about 1.5 million volts and having a power output of approximately half a kilowatt. Ruggedness, simplicity, and economy have been important considerations in the design. The generator is of the belt type (see preceding abstract), the electrodes consisting of spun aluminum spheres two feet in diameter. Each sphere is supported on an insulating column three feet long and one foot in diameter. Maintenance of warm dry air within the columns insures independence of atmospheric conditions, while a helical india ink leak along the surface of each column insures a uniform potential gradient between sphere and ground. A rigid box-like structure of steel serves as a base, and the entire assembly, having an overall height of seven feet, is mounted on large rubber-tired casters.

55. The initiation of discharges in high vacua. J. W. BEAMS, *University of Virginia.*—Surge potentials (of about 10^{-6} sec. duration) were applied to point-plane or wire-cylinder electrodes in high vacua, and the conditions of

* Invited paper.

breakdown studied. (For method see Phys. Rev. **41**, 687 (1932)). The smaller electrode was of Pt, W, or steel; the larger of Ni or steel. When the point or wire was negative it was found that the discharge was started by the field electron current from the cold cathode. (See Wood, Phys. Rev. **5**, 1 (1897), Hull and Burger, Phys. Rev. **31**, 1121 (1928), Snoddy, Phys. Rev. **37**, 1678 (1931).) With point or wire positive, however, and plane or cylinder grounded, discharges were observed to occur when the maximum field at the cathode was much lower than usually believed to be necessary in order to produce sufficient field electron current to start the discharge. This discharge potential was raised by heating the anode, by baking out the complete tube or by allowing several discharges to pass. The evidence indicates that these discharges are initiated by positive ions pulled out of the point or wire anode by the electric field.

56. The effect of high electrostatic fields upon the vaporization of molybdenum. G. B. ESTABROOK, *University of Pittsburgh.* (*Introduced by A. G. Worthing.*)—It has been found for wires of varying diameters, (1) that, for field strengths of about 0.52×10^6 volts/cm or less at the wire surface, there was no change in the rate of change of resistance with time and hence the rate of vaporization upon application of the field; (2) that, for field strengths above approximately 0.52×10^6 volts/cm, as successively higher fields were applied, the rate of vaporization first decreased slowly, then more rapidly, and finally asymptotically toward zero at field strength over 1.8×10^6 volts/cm; (3) that, with increasing temperatures, the same field strength applied at the surface of a wire produced progressively smaller decreases in the rate of vaporization; (4) that, when there was an effect upon the rate of vaporization, sudden increases in resistance occurred when the field was applied, and sudden decreases when it was removed. A decrease in vaporization rates was found for platinum, along with a sudden increase in resistance upon applying the field, and a sudden decrease when the field was removed. Worthing has reported similar results for tungsten except that the sudden increases and decreases were opposite to those of platinum and molybdenum.

57. On the effect of high electrostatic fields on the vaporization of metals. A. G. WORTHING, *University of Pittsburgh.*—Work with tungsten and molybdenum (see preceding abstract) shows that their vaporization rates may be altered greatly by electrostatic fields. Obviously there may be involved either the recapture by the external field of material vaporized presumably as dipoles, the actual prevention of vaporization, or both. Recapture of material vaporized as atoms on the dipole assumption alone fails because of the huge polarizabilities required. Recapture of material vaporized as large aggregations of atoms fails because the effect actually becomes appreciable only at fields of the order of a million volts per cm, though the prevention of vaporization is almost complete at fields three or four times this value. Production of electrostatically oriented surface layers of dipoles with consequent strengthening of the external field, similar to the strengthening of an external magnetic field by ferromagnetic material, with consequent recapture of vaporized materials fails quantitatively. The foregoing seems to exhaust possibilities of classical explanations of this effect. Further consideration is being given on the basis of quantum mechanics.

58. Interference of light in transparent films of manganese. J. B. NATHANSON, *Carnegie Institute of Technology.*—Transparent films of manganese of variable thickness were obtained by sputtering manganese on Pyrex glass plates. The manganese cathode was totally enclosed in mica except for a circular opening 1.5 cm in diameter, facing the glass plate. When the films were examined in monochromatic light, a series of dark circular fringes were observed similar to Newton's rings. Examination showed no deposit of manganese in the small region directly opposite to the center of the opening in the mica. A section of the film taken perpendicular to its face would therefore be similar to that of a vertical section of a volcano. Employing the wavelength of monochromatic light in the metal as a means for thickness measurements, the average thickness of the film was evaluated graphically from the diameters of the interference rings. Measurements were made for light of wavelengths 5461A and 5893A. Two different films were measured, having maximum thicknesses of 7×10^{-5} cm and 8×10^{-5} cm respectively. The masses of the films were computed from the average thickness of the films and the density of manganese. A comparison of the computed masses with those obtained by weighing of the glass plates before and after sputtering, showed differences not exceeding 14%. The phenomenon described also suggests the possibility of evaluating the refractive indices of metals in thin films.

59. Resistivity of expanded conductors. P. I. WOLD, *Union College.*—In connection with certain work on the Hall effect it became important to know how the resistivity of a conductor is affected by the presence of a large number of gas bubbles or other insulating material. Measurements were taken on a form of Hg obtained from an ammonium amalgam. The Hg is expanded with numerous bubbles of gas of various sizes and in disorganized array. Lord Rayleigh has considered the case of a rectangular array of uniform insulating spheres in a conducting matrix and gives the approximate formula $\sigma=(1+\frac{1}{2}p)/(1-p)$ or $p_1=(2\sigma-2)/(2\sigma+1)$ where $\sigma=R_2/R_1$; R_2 and R_1 are the resistances with and without spheres and p is the fractional volume occupied by the spheres. This is found to hold fairly well for $p<0.2$. Many measurements were taken on sand, of approximate sphericity, in $CuSO_4$ solution and for which $p=0.7$ about. For these values the simple formula breaks down. A modified formula bringing in the next term in a series has been derived which gives

$$p_2=p_1[1-0.196p_2^{10/3}],$$

where p_2 is the new or corrected value. A double application of this last relation gives (for p as high as 0.75) values correct to 1/2%. For lower values of p the accuracy is higher. Fricke has derived a formula which takes into consideration the nonsphericity of the particles and which, for spheres, reduces to Rayleigh's simple formula. The present

work indicates that, except possibly in extreme departure from sphericity, Fricke's correction is not so important as that given above.

60. Absorption and reradiation of short electric waves. C. R. FOUNTAIN, *George Peabody College for Teachers, Nashville, Tennessee.*—Radiations from a short wave transmitter (3.7 meters) are absorbed and reradiated by a resonance rod at various positions in the field. The quantity of energy reradiated is vastly greater than seems possible by classical wave theories, yet beautiful interference curves are obtained by moving the rod. The human body also reradiates such waves, requiring all energy observations to be read through a telescope 75 feet from the transmitter. The magnitude of the effect is shown by a "swinging curve," with receiver stationary at 12.6 meters from the transmitter while the resonance rod is swung around the transmitter in a circle of 12.6 meters radius. Maxima came at the following distances from the receiver: 2.44 meters (182%), 6.20 meters (137%) 10.00 meters (125%). Minima occurred at 4.50 meters (67%), 8.18 meters (83%). "Rod removed" was considered 100%. If the slender rod, 12.6 meters from the transmitter, is to supply 25% more energy to the receiver, 10 meters away, it must gather in and reradiate all the energy radiated from the transmitter through an angle of 72°, a path 4 waves wide. The bunching of energy, as in the photoelectric effect, seems to exist with waves 3.7 meters long.

61. A search for a new gyromagnetic effect: Magnetization by the rotation of a magnetic field. S. J. BARNETT, *University of California at Los Angeles and California Institute of Technology.*—In 1925 J. W. Fisher, in London, made experiments in which a magnetic rod at rest was crossed by a weak magnetic field produced and rotated by a two phase electrical system. He expected the magnetic elements to be rotated with the field, and the rod itself to become (gyrostatically) magnetized exactly as if itself were in rotation with the same frequency (Barnett effect). The null effect obtained led him to conclude that no mean rotation of the elements with the field occurred. I showed, however (Phys. Rev., 1925), that on the most favorable hypotheses Fisher's expectation should be greatly reduced by multiplication with a factor approximately 1.5 times the cross magnetization ÷ the saturation magnetization. Fisher's errors were of the same order as this reduced result. A new investigation of this subject, going much further than Fisher's, has now been made, with rods of iron and permalloy dust in impressed fields with intensity 15 gauss rotating at about 15,000 revolutions per second. The mean magnetometer deflection on double reversal of the rotation was about 0.2 mm (in the wrong direction), mean error about 1 mm; while the deflections predicted from the modified formula were about 4 cm and 1.5 cm for permalloy and iron, respectively. Fisher's formula, or the Barnett effect, would give about 10 meters and 7 meters, respectively. It is thus clear that either (1) no appreciable rotation of the elements occurs in weak fields, or (2) if such rotation occurs the molecular torques opposing axial alignment are much greater (as would be expected) when the field rotates than when the rod rotates.

62. The gyromagnetic ratios for nickel and cobalt. S. J. BARNETT, *University of California at Los Angeles and California Institute of Technology.*—In an elaborate investigation of the rotation of both iron and permalloy by magnetization (Proc. Amer. Acad. 66, No. 8) the gyromagnetic ratios for the two substances were found to be, respectively, $1.04\times m/e$ and $1.05\times m/e$, with errors probably less than one-half percent. Successful observations have now been made on the less tractable substances nickel and cobalt, but the results are somewhat less precise. The ratios obtained for those substances are about $1.06\times m/e$ and $1.07\times m/e$. The experimental method had to be modified to reduce the effects of certain sources of error, including magnetostriction, before any success was obtained with cobalt. Inasmuch as serious errors, not suspected by other investigators, have been eliminated in all of this work the results obtained are far more reliable than those obtained by others, who have always obtained $1\times m/e$ within the limits of their supposed experimental errors (except Einstein and de Haas, who, in 1915, thought they had found $2\times m/e$). The ratios obtained in this investigation agree, within the experimental error, with those published by L. J. H. Barnett and myself in 1925 (Proc. Amer. Acad. 60, No. 2) as the result of an elaborate investigation of the magnetization of many ferromagnetic substances by rotation. The mean then obtained was $1.06\times m/e$, with an error estimated as some two percent.

63. Probabilities of *K*-electron ionization of silver by cathode rays. D. L. WEBSTER, W. W. HANSEN, AND F. B. DUVENECK, *Stanford University.*—These probabilities are measured by K line intensities from thin films. Preliminary data with Ag on a Be block (Phys. Rev. **42**, 141L (1932)) are confirmed, and a first approximation for the correction for fluorescence under Be continuous rays is replaced by more exact calculations. Since these increase the correction considerably, we have also taken data on Ag without Be, giving approximately the same results. Defining U as V/V_K and taking intensities at $U=2$ as unity, results to date indicate intensity 0.745 at $U=1.5$, 1.13 at 3, 1.12 at 5, 1.06 at 7. Available wave-mechanical theories depend on Born's approximation, invalid unless U is large. Classical quantum theory appears best expressed by multiplying Thomas's formula by a factor for convergence of possible cathode-ray paths approaching a nucleus, giving

$$\text{Probability}=\frac{\text{constant}}{U}\left\{1-\frac{1}{U}+\frac{2K}{3}\left(1-\frac{1}{U^2}\right)\right\},$$

where $eV_KK=$orbital kinetic energy. This departs so far from experiment as to prove strictly classical postulates unsatisfactory even as temporary approximations. Heuristic theories can be formulated by modifying the law of repulsion (l.c.), but the trouble probably lies in the fundamental defect of any classical theory, in contradicting the indeterminacy principle.

64. Relative intensity of the silver *K*-lines from a thick target as a function of voltage and emergence angle. D. L. WEBSTER, W. W. HANSEN, AND F. B. DUVENECK, *Stanford University.*—The *K*-line intensity from a thick silver target has been measured in arbitrary units for voltages up to 180 kv with emergence angles from 1° to 25°. A practical use of these data is the determination of the voltage which will give the maximum line x-ray efficiency at any emergence angle. At 1°, the best voltage is 70 kv, but at 25° it is well above 180 kv. These data may also be used in conjunction with results on thin targets (preceding abstract) to get information as to the retardation of cathode rays in silver. For this purpose the data are corrected to eliminate the effects of target absorption (by Kulenkampff's method) and of rediffusion (Phys. Rev. **37**, 115 (1931)). We find that the cathode-ray retardation law can be represented by the formula $dT/ds = -\text{const.}/T^{0.5}$ where T is the kinetic energy of the electron, and s is distance along the cathode-ray path. The above result agrees within our rather large limits of error with more direct tests (as summarized by Williams). Reversing the logic it seems likely that thick target emission phenomena can be completely explained by the laws of thin target emission, cathode-ray retardation and rediffusion, and x-ray absorption.

65. Comparison of the angular distributions of the cosmic radiation at elevations 6280 ft. and 620 ft. THOMAS H. JOHNSON, *Bartol Research Foundation of the Franklin Institute.*—The ray intensity $j(\theta)$ of the cosmic radiation has been studied as a function of the angle θ from the vertical on Mt. Washington, N. H., elevation 6280 ft., and at a base station, elevation 620 ft. The results show a distribution less concentrated about the vertical at the higher elevation. Unless some *ad hoc* assumption is invoked this result is inconsistent with the intensities and absorption coefficients deduced by Millikan and Cameron as their results would lead to a considerably more concentrated distribution at the upper elevation. Integrating the ray intensities over all angles, the total numbers of rays per cm^2 per sec. have been computed at the two elevations. The increase in the number of rays with elevation is less than the known increase in the ionization (Millikan and Cameron). The ratio of numbers of rays per sec. is 1.46 against 1.87 for the ratio of ionizations at the two elevations. The average 6280 ft. ray, therefore, produces 1.28 as many ions per unit path as the 620 ft. ray. This change in ionizing efficiency may perhaps be explained by supposing that the rays of the softer components which predominate at the upper level occur more frequently in associated groups.

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